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16. Abstracts

The results are reported of technical and economic evaluations of the feasibility of different SO_2-control processes. In addition to process evaluations, studies were made of; the applicability of these processes to both power plants and SO_2-control processes, and the impact SO_2-control technology would have on emission reduction. Preliminary process designs and economic evaluations have been prepared for twelve different SO_2-control processes. Investments are reported in millions of dollars for a 1,000 MW plant so the investment cost in dollars per Kilowatt has the same value. The operating costs are reported as dollars per ton of sulfur not emitted, as mills per Kilowatt-hour, and as a percent increase of power cost. Of the twelve processes evaluated, none can be ranked as commercially available at the present time.

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EVALUATION OF SO_2-CONTROL PROCESSES

TASK #5 FINAL REPORT

Submitted to
ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF AIR PROGRAMS
DIVISION OF CONTROL SYSTEMS
Contract No. CPA 70-68

APPROVED: Arthur G. Sliger
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THE M. W. KELLOGG COMPANY
A DIVISION OF PULLMAN INCORPORATED

Research & Engineering Development

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TASK #5 FINAL REPORT

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EVALUATION OF SO_2-CONTROL PROCESSES

TASK #5 FINAL REPORT

CONTRACT NO. CPA 70-68

Submitted to

ENVIRONMENTAL PROTECTION AGENCY

OFFICE OF AIR PROGRAMS

DIVISION OF CONTROL SYSTEMS

by

THE M. W. KELLOGG COMPANY
RESEARCH & ENGINEERING DEVELOPMENT
PISCATAWAY, N.J.

October 15, 1971

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I. PREFACE

The major objective of the work described in this report was to provide APCO with a consistent basis for comparing the feasibility of different SO_2- control processes, both technically and economically. Neither time, funds, nor input data were available to permit a detailed evaluation of each process to be made and the results of this study should not, therefore, be used without considering their limitations. The major use for these results is expected to be in process screening and program planning in which case the relative rather than absolute merits of the processes will be of prime importance. Since the accuracy of the estimates is higher on a comparative basis than it is on an absolute scale, it is felt that the results do, in fact, provide a sound basis for program planning.

It should not be construed from the above discussion that the individual estimates for the various processes are so inaccurate as to be meaningless on an absolute basis. The estimating accuracy itself, based on the flow sheets as shown, is judged to be within about 30%. It is the lack of detailed process design for each case that creates the most uncertainty and this uncertainty will vary among the different processes evaluated according to the status of the input data for each. Based on past experience, it has been found, without exception, that for a first-of-a-kind plant, the estimated investment increases as more data become available up to the point where a definitive detailed design can be made. Thus, in the present study, the estimated investments of those processes for which the most data are available (e.g., molten carbonate) will be much closer to the actual cost than those based on very little data (e.g., potassium formate). In all cases, however, the investments presented in this report will be lower than the actual cost of the first plant built for reasons given below, excluding any increases owing to inflation.

- The investments included in this report are essentially for battery limits plants only and therefore do not represent complete plant costs. However, for those processes producing byproduct acid, storage tanks have been included.
- The design basis assumed that technology was well established in each case and safety factors (e.g., gas bypasses) were not needed.
- New power plants only were considered, no retrofits.
- Waste disposal was treated as an operating cost (e.g., 50¢/ton) whereas in some cases it could increase the investment significantly.
- Items such as interest during construction, start-up costs, and working capital were not included.
- No contingencies were included.
- Detailed designs and cost estimates were not prepared for a specific installation; rather a general case was used.
- The process design used in each case does not necessarily reflect the latest data since these were not always available at the time of the study. In many cases, the data used did not come directly from the developer of the process but from other sources such as published papers.

Since many of the factors that influence complete plant investment were not used in developing the present costs, in no case should any of the investments reported herein be compared with a definitive estimate prepared from a detailed design for a specific installation.

As previously stated, the main objective of this study was to provide a sound basis for program planning and thereby to allow more selective funding of processes. A second phase tentatively was planned whereby the most promising candidates from this first study would be evaluated in greater depth to obtain investments for complete plants, rather than battery limits only, and thus provide costs that would more closely approach the actual costs. These latter costs can, of course, be obtained only by preparing a detailed design and definitive estimate for a specific installation for each process considered. To follow this latter procedure for a number of different processes would require a very large expenditure of man-hours and money and also would require the availability of input data needed for a detailed process design.

Within the limitations imposed by the ground rules of the study, the results reported herein do provide a reasonably accurate comparison of the candidate SO_2-control process. In addition, the values reported may be used as indicative of the actual investments required with the qualification noted above that they are low since they represent battery limit designs rather than complete plants.

Operating costs for each process are reported based on a format derived during the course of the study. Since investment contributes significantly to operating costs, probably these also are lower than will be obtained in an actual case, provided the other assumptions (chemical cost, capital charge rate, depreciation, etc.) are correct. In any event, it is extremely doubtful that the reported costs will be lower than shown and more likely, will be higher. More exact operating costs can be estimated after definitive designs are prepared.

II. INTRODUCTION

The work reported on herein was performed pursuant to Contract No. CPA 70-68 with the Air Pollution Control Office (APCO)*, Environmental Protection Agency (EPA). The task specifications were delineated by APCO in Task No. 5 Contract Task Specification Request, dated January 27, 1971, Task Change No. 1, February 4, 1971, and Task Change No. 2, March 12, 1971.

Task Order No. 5, in short, specified that estimates of plant investment were to be made for several different SO_2-control processes. The processes to be evaluated were to be specified by APCO and all input process data for preparing the estimates likewise were to be furnished by APCO. In addition to the process evaluations, other items to be studied were applicability of these processes to power generating stations, a time schedule relating to the construction of both power plants and SO_2- control processes, and the impact SO_2- control technology would have on emission reduction. APCO also requested Kellogg to comment on advanced power cycle technology based on a United Aircraft report.

The primary objective of this work was to develop a sound basis for APCO to use in determining which of the many proposed processes they should support. Specifically, APCO had to prepare a five-year plan for SO_2- control process development and to insure that priorities were properly assigned, they needed technical and economic evaluations of the leading candidates on a consistent basis. To achieve the desired objective within the time and funds allocated, certain "ground rules" were established that were to be followed throughout the study. These are tabulated below.

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* Since changed to Office of Air Programs (OAP).

- A single size (1,000 MW) new power plant would be assumed for all processes except Dry Limestone Injection which was set at 350 MW.

- All input data were to be supplied by APCO (see Section IV A. 1. for a listing of the input data actually received and used).

- No process optimizations were to be made by M. W. Kellogg; instead the process design in each case would be used as received from APCO. Only those changes would be made that were necessary to 1) convert the process to the standard design bases; or 2) make the process feasible if, based on either judgment or data, it appeared the base design was inoperable.

- Approximate plant investments were to be estimated for each case. Since neither time nor input data permitted a detailed design and estimate to be made, it was recognized that the accuracy of the individual estimates would suffer but the relative comparative accuracy should be much higher.

- Operating costs would be calculated for each case with the various parameters (e.g., capital charge rate, utility charges, etc.) to be specified during the course of the task.

- The final results to include major equipment costs and total investment with the operating costs shown in detail. Additional discussion of the estimating procedure is included in Section II. A. 2. of this report.

- The entire task, including the Applicability Survey, initially was scheduled for completion in three months (by April 26, 1971) but was later extended to four months (to May 31, 1971 completion date).

In many cases the input data received were insufficient for a process design and for these, additional data were obtained from the general literature whenever possible. If literature data were not available then assumptions were made as required to complete the design. It was recognized that while this may not be the most desirable procedure, within the time and funds allocated for the task, it was the only method that could be used. It is tentatively planned to make a more detailed evaluation for those processes which appeared to have the best technical and economic potential based on the results of the present study.

III. SUMMARY

Preliminary process designs and economic evaluations have been prepared for twelve different SO_2- control processes. The process economics are summarized in Table 1. Investments are reported in millions of dollars for a 1,000 MW plant (except for dry limestone) so the investment cost in dollars per kilowatt has the same value; i.e., a 20 million dollar investment for a 1,000 MW plant is equivalent to 20 dollars per kilowatt. The actual investments range from a low of $9.7/KW for dry limestone injection to a high of $43.4/KW for the Cat-Ox process.

The operating costs are reported as dollars per ton of sulfur not emitted, as mills per kilowatt-hour, and as a percent increase of power cost. All of these costs are shown as gross (excluding byproduct credit) and net (including byproduct credit). In the "throwaway" processes there is, of course, no difference in the gross and net since no salable byproduct is produced. Further, the base case ammonia scrubbing process is treated differently since the ammonium sulfate formed in the scrubber ultimately is used to produce fertilizer. This latter process is divided into two sections, viz, gas scrubbing and fertilizer production. The areas of primary interest for this study are the gas scrubbing costs and these are shown as gross costs in Table 1.

Since the primary purpose of the power plant is to generate power (presumably at the lowest cost), it would seem that the major concern with the SO_2- control processes would be the resulting increase in power cost. The cost of the sulfur not emitted provides a convenient means of comparing processes but if the design conditions are not

TABLE

SO$_2$ REMOVAL PROCESSES - EC

	Limestone Wet Scrubbing	Limestone Dry Injection	Cat-Ox
Plant Size (MW)	1000	350	1000
Percent of Sulfur Removed From Flue Gas	90	50	90
Fixed Capital Investment ($MM)	10.8	3.4	43.4
Salable By-Product	None	None	(78% (H_2SO_4
By-Product Production (Tons/Day)	-	-	1061
By-Product Credit ($MM/Yr)	-	-	1.45
Total Gross Production Cost ($MM/Yr)	5.14	1.72	12.48
$/Ton Sulfur Not Emitted	65.2	112.2	158.0
Mills/KWH	0.73	0.70	1.78
% Increase of Power Cost	10.8	10.4	26.4
Total Net Production Cost ($MM/Yr)	-	-	10.58
$/Ton Sulfur Not Emitted	-	-	133.9
Mills/KWH	-	-	1.51
% Increase of Power Cost	-	-	22.4

Notes:

By-Product Values
78-80% Sulfuric Acid - $6/Ton 100% Contained
98.5% Sulfuric Acid - $12/Ton
60% Nitric Acid - $25/Ton 100%
Sulfur - $20/Short Ton
Plant Load Factor - 80% (7000 hr Stream Year)
Electric Power Manufacturing Cost - 6.75 Mills/KWH
Plant Location - Cincinnati, Ohio

* Ammonia Sc

$(NH_4)_2SO$

Fertilizer
Investme

Gross Pr
MM$/Ye
$/Ton

ABLE 1

- ECONOMICS SUMMARY SHEET

ox	Molten Carbonate	Potassium Formate	Ammonia Scrubbing (Base)	Ammonia Scrubbing (A) (Steam Stripping)	Ammonia Scrubbing (B) (Thermal Decomposition)	Tyco	Magnesium Oxide Scrubbing	Zinc Oxide	Citrate
	1000	1000	1000	1000	1000	1000	1000	1000	1000
	95	90	90	90	90	87.5	95	90	90
	34.6	34.9	10.2	16.2	21.6	29.8	26.8	21.8	21.2
				(98.5%	(98.5%	(80%H_2SO_4	(98.5%	(98.5%	
	Sulfur	Sulfur	*	(H_2SO_4	(H_2SO_4	(60%HNO_3	(H_2SO_4	(H_2SO_4	Sulfur
	261	245		570	692	971 H_2SO_4 148 HNO_3	890	754	251
	1.52	1.43		2.00	2.42	1.36) 0.65)2.01	3.12	2.64	1.46
	12.32	13.32	9.98	7.86	8.38	10.51	9.04	7.73	7.75
	148.4	169.3	126.8	99.9	106.6	137.7	111.1	98.1	98.3
	1.76	1.90	1.43	1.12	1.20	1.50	1.29	1.10	1.11
	26.1	28.1	21.2	16.6	17.8	22.2	19.1	16.3	16.4
	10.80	11.89	-	5.86	5.96	8.03	5.93	5.09	6.29
	130.1	150.7	-	74.3	75.5	104.7	71.3	64.4	79.4
	1.54	1.70	-	0.84	0.85	1.15	0.85	0.73	0.90
	22.8	25.2	-	12.4	12.6	17.0	12.6	10.8	13.3

ia Scrubbing (Base)

)$_2SO_4$ Prod. Cost - $30.80/Ton Transfer Price

lizer Plant (incl. HNO_3 Plant)
stment $28.0 MM

ss Production Cost
M$/Year 36.51
/Ton Fertilizer 52.82

B

identical among processes the cost of not emitting sulfur may not indicate accurately the increase in power costs. For example, if the cost of not emitting sulfur is plotted against the percent increase in power cost, a straight line can be drawn through all points except dry limestone. This latter process is for a smaller plant and removes only 50% of the sulfur from the flue gas whereas the others remove 90%. Thus, caution should be exercised when comparing different processes on a cost of sulfur not emitted basis.

Of the twelve processes evaluated, none can be ranked as commercially available at the present time. Wet limestone has been tested in a 100 MW unit, dry limestone is presently being evaluated in a 150 MW plant, Cat-Ox has undergone pilot plant testing (≃15 MW), and it and several others are presently being installed in power plants of about 100 MW capacity or higher. However, the results currently available to Kellogg for the present study are insufficient to allow an assessment as to whether adequate data exist to permit a full size commercial plant to be designed and built with a high level of confidence. Some processes have been developed more than others while some that are more advanced could not be fully evaluated owing to data unavailability.

IV. BASIS OF EVALUATION

The results of the Applicability Survey have been reported separately and therefore will not be repeated here.

A. Process

1. Input Data

The twelve SO_2- control processes for which APCO requested evaluations are listed below along with the input data received for each.

1) Wet Limestone Scrubbing - TVA Conceptual Design and Cost Study Series Report, Study No. 2, 1969.

2) Dry Limestone Injection - TVA Conceptual Design and Cost Study Series Report, Study No. 1, 1968.

3) Cat-Ox (Monsanto) - an SRI final report covering their evaluation of the process under Contract CPA 22-69-68.

4) Molten Salt (Atomics International) - seven AI reports containing exploratory data, the latest dated 1969. A Singmaster & Breyer report showing the design and estimate of a unit sized for an 800 MW power plant.

5) Formate Process (Consolidation Coal) - Paper presented at the 1970 ACS meeting in Houston.

6) Ammonia Scrubbing (Base Case - fertilizer production) - TVA Conceptual Design and Cost Study Series Report, Study No. 3, 1970.

7) Ammonia Scrubbing (Alternate A - Steam Stripping) - same as 6. Plus some additional data from TVA's pilot plant.

8) Ammonia Scrubbing (Alternate B - Thermal Decomposition) - same as 7.

9) Modified Chamber Process (TYCO) - TVA report covering Preliminary Conceptual Design and Cost Study; A.M. Kinney, Inc. report on heat and material balance analysis; TYCO final report, Contract CPA 70-59, April-October 1970.

10) Magnesium Oxide Scrubbing - Experimental data from Babcock and Wilcox, Report 5153, September 1970, and a block type flow sheet of a conceptual design.

11) Zinc Oxide Scrubbing - Final report by the Envirogenics Company (Div. of Aerojet-General Corp.) for Contract PH 86-68-77, October 1970.

12) Citrate Process (USBM) - Status report from the Bureau of Mines, January 1971.

2. Design Bases

Since a major objective of the present study was to compare all the different processes on a uniform basis, it was imperative that the same design bases be used for the parameters common to all processes. Accordingly, the bases shown in Table 2 were specified and used in this study. Design parameters peculiar to each process are given in the individual reports included as Section IX, the Appendix of this report.

A plant site in Cincinnati, Ohio was selected for the evaluations since this general area contains a number of large power plants and extensive coal deposits are nearby. (A map showing the location of the major thermal power plants in the United States is included in the Applicability Survey report.) A coal sulfur content of 3.5% was desired as the power plant fuel and a coal meeting this requirement was shown for Harrison County, Ohio, in Table 1, Page 13, of USBM RI 7346, "Analyses of Tipple and Delivered Samples of Coals," 1970. Since only the proximate analysis is given, the composition was adjusted slightly to match the reported heating value. Flue gas quantity was calculated using 20% excess air which was assumed to be at 80°F with a relative humidity of 60%. A heat rate of 9,000 Btu/kwh was chosen as a reasonable value for a new large power plant.

To simplify the process calculations, it was assumed that all of the coal sulfur would appear in the flue gas (i.e., no sulfur left in the ash) with 98% forming SO_2 and the remaining 2% present as SO_3. A nominal SO_2- removal of 90% was specified for all processes but the actual removal varied slightly owing to the inherent differences among the processes.

Table 2

GENERAL PROCESS DESIGN BASES

Coal Composition

Component	Dry Wt. %
Ash	15.2
S	3.5
H_2	5.0
C	67.2
N	1.6
O	7.5
Water in Coal	4.8 Lbs/100 Lbs Wet

Excess Air	20%
Carbon Burned in Coal	100%
Heating Value in Coal	
Wet	11,980 Btu/Lb
Dry	12,580 Btu/Lb
Sulfur to SO_2	98%
Sulfur to SO_3	2%
SO_2 Removal	90%
Flue Gas Temperature Out of Air Preheater	300°F
Minimum Gas Temperature to Stack After Treatment	200°F
Preferable Gas Temperature to Stack After Treatment	250°F or Higher
Gas Velocities in Ducts	60 Ft/Sec
Plant Size	1,000 MW
Heat Rate	9,000 Btu/Kwhr
Flue Gas Quantity	293,000 Moles/Hr
Flue Gas Molecular Weight	29.54
Flue Gas Weight	8,655,000 Lbs/Hr

Flue Gas Composition

Component	Mole Fraction
SO_2	0.00261
SO_3	0.00005
CO_2	0.13657
N_2	0.74087
O_2	0.03276
H_2O	0.08714
Fly Ash	77,900 Lbs/Hr

Water in Air (60% RH @ 80°F)	0.0212 Mols/Mol Dry Air
Coal Consumption Rate (Wet)	751,252 Lbs/Hr

Gas ducts 300°F or higher to be insulated.

A preferable stack gas exit temperature of 250°F was selected based on a TVA study, "Use of Limestone in Wet-Scrubbing Process," Conceptual Design and Cost Study Series, Study No. 2, 1969. While opinions vary widely among power producers as to the optimum exit temperature, the 250°F value seemed reasonable at the time this study was made. Also, since all processes are designed using the same basis, the relative comparisons should not change appreciably at other exit temperatures. The effect of reheat temperature on process costs should be studied in more detail when the process evaluations are extended.

The gas velocity in the ducts was specified as a nominal 60 feet per second based on verbal information from various power plant designers. The recommended velocities ranged from about 40 to 120 feet/second with a nominal value of 4,000 feet/minute frequently quoted. Thus the design figure of 60 feet/second actually used falls within the normal range and is a reasonable value for the present study. A more complete study might require optimization of gas velocity -- balancing lower investment against higher pressure drop, hence operating cost, as the velocity increases -- but this was beyond the scope of the present evaluation.

The percentage of the total ash in the coal that appears as fly ash generally falls within the range of 60-85. For this study it was assumed that the quantity of fly ash produced would fall about midrange.

The values shown in Table 2 formed the basis for the process design in each case except as noted in the individual discussions. Material balances which were received as part of the input data were converted to these bases or, if none were received, process balances were made using Table 2 values.

B. Estimating

The present estimates are classified as approximate owing to the limited data available and the special nature of the equipment involved but are felt to represent the best quality that could be prepared within the calendar time and man-hours available. It should be noted that the estimates contain many large cost items, the prices of which in some cases have been established by an estimator's judgment only since sufficient data and time were not available to develop any better pricing. Further, the purchased cost of a large item in many cases was obtained by contacting a single vendor for a budget type quote and it is doubtful if the optimum cost and/or design was always obtained. Also, since some process items were ill-defined (data lacking or proprietary and unavailable), they had to be treated as "black boxes" and the resulting costs could be quite inaccurate.

Owing to the reasons cited above, it is difficult to properly judge the accuracy of the present estimates. Nevertheless, some indication of accuracy is required and, therefore, the following appraisal is offered. It is felt that the accuracy of the present estimates is no better than 30% and could be poorer. However, since all of the estimates were prepared essentially simultaneously in a single department and some of the equipment is similar, the relative comparative accuracy probably is better than the accuracy of any one plant. It should be noted that, based on past experience, costs invariably increase as more data become available. It is reasonable to assume, therefore, that the present costs, which are based on processes not yet completely developed, would increase rather than decrease as more detailed evaluations are made. Accordingly, the cited accuracy of 30% should not be considered as a plus or minus value since more likely it would be in the -5 to +25% range. The degree of the expected cost increases would, of course, vary from process to process generally as a function of the status of the input data.

The estimates as reported in the next section of this report do not include contingency nor undeveloped design allowance (UDA). Neither do they represent complete plant investments since a number of items are not included such as inventory, interest during construction, working capital, cost of land, nor offsites such as laboratories, site preparation, access roads, and incremental costs of maintenance shops and warehouses. These items have not been included since they are relatively small compared to the total investment and would have no significant effect on the comparisons. Therefore, it was decided that the time required for including the items necessary to obtain a complete plant investment was not justified in view of the very limited overall schedule. These items can be added when more detailed estimates are made.

The general bases used in preparing the estimates are as follows. The plant site selected was Cincinnati, Ohio, as previously mentioned, and labor productivity and rates for this area were obtained. Thus the total investments reported herein would be somewhat different for other locations.

The general rationale followed was to charge the SO_2-control process for all costs that resulted, directly or indirectly, from the installation of the process. Thus increased costs of ductwork, flue gas fans, and dust removal equipment were considered to be part of the control process. To insure that proper charges were made in all cases, a "standard" power plant design was used to determine the investment for the items cited above and allowances for these items were then credited to the control process. (Basis for the standard power plant was TVA's Bull Run Steam Plant which has a unit nameplate rating of 950 MW.) For example, the weight of the standard plant ductwork was determined (by designing the ducts and making a layout) and this was subtracted from the total ductwork weight required when an SO_2- control process was added.

The incremental fan horsepower required by the control process was calculated from the total gas flow and increased pressure drop which is caused by the additional ducts and equipment.

The incremental cost of the dust removal equipment, assumed to be an electrostatic precipitator (ESP), required that a "standard" be specified for the power plant. Since the requirements were not well-defined, two different base case ESP's were estimated: one at 95% overall dust removal efficiency and one at 99%. The effect of each of these is shown in the process investments. If the process itself removes the fly ash then a credit is taken for eliminating the ESP. On the other hand, if the process requires an unusually high dust removal efficiency (e.g. 99.5% minimum), then the increased cost of the more efficient unit is added to the process investment. These conditions apply only to a new plant since no credit could be taken for an existing ESP nor would the incremental costs of increasing efficiency be the same in an existing plant.

Equipment needed for by-product recovery, i.e., acid plants or Claus plants, are included as part of the process investment. When acid is produced, a nominal 30 days storage has been provided to insure continuity of operation even when faced with short-term delays such as temporary loss of tank cars or trucks, rail strikes lasting a few days, etc.

One important point in the design rationale that should be noted is that no by-passes have been provided around the process units. If these were required, the cost would increase in all cases. Provisions have been made, however, for shutting off one complete train of process equipment which provides some flexibility since multiple trains are required in all cases.

V. RESULTS

A. Investment

The estimated investment for each of the twelve processes evaluated is tabulated below. Note that the dry limestone process is for a 350 MW plant but all the others are based on a 1,000 MW plant. A detailed breakdown of the investment costs is shown in Table 3. For convenience the major assumptions and major changes to process designs received as input data are summarized in Table 4. For complete bases see Table 2 and the individual discussions for each process given in the Appendix of this report.

PROCESS	INVESTMENT, $	$/KW
1. Wet Limestone Scrubbing	10,800,000	10.8
2. Dry Limestone Injection	3,400,000	9.7
3. Cat-Ox	43,400,000	43.4
4. Molten Salt	34,600,000	34.6
5. Formate	34,900,000	34.9
6. Ammonia Scrubbing (Fertilizer)	38,200,000	38.2
7. Ammonia Scrubbing (Steam Stripping)	16,200,000	16.2
8. Ammonia Scrubbing (Thermal Decomposition)	21,600,000	21.6
9. Tyco	29,800,000	29.8
10. Magnesium Oxide Scrubbing	26,800,000	26.8
11. Zinc Oxide Scrubbing	21,800,000	21.8
12. Citrate	21,200,000	21.2

As previously mentioned, all of the wet scrubbing processes have a gas reheat system designed to produce a stack gas temperature of 250°F. The system selected was based on a TVA study and for their conditions gave the lowest costs. However, it appears that the carbon steel material of construction specified for the exchanger downstream of the air preheater (i.e., upstream of the gas scrubber) is inadequate since the gas will be cooled below

SO

	Limestone Wet Scrubbing	Limestone Dry Injection	Cat-Ox
Major Equipment Cost			
Direct Materials	5,395	664	13,525(c)
Sub-Contracts	324	91	1,360
Ductwork, Duct Valves, and Expansion Joints	937	124	4,231(a)
Piping, Electrical & Instruments	1,323	166	1,940
Foundations, Concrete & Steel Structures, Buildings, Paint, and Insulation			
Direct Materials	340	76	440
Sub-Contracts	170	70	340
Subtotal - Materials & Sub-Contracts	8,489	1,191	21,836
Other Costs			
Construction Forces, Home Office Engineering, Procurement, Insurance, Start-up and Contractor's Fee	6,711	1,409	17,064
Investment Cost for Reforming Unit, Oxygen Plant & K_2SO_3 Recovery			
Subtotal Investment Cost for Process Plant	15,200	2,600	38,900
Other Process Units Investment Costs			
Claus Sulfur Plant			
Sulfuric Acid Plant Including Sulfuric Acid Storage			1,400(b)
Fertilizer Plant Including Storage and Nitric Acid Plant			
Electrostatic Precipitator		2,400(e)	7,500(f)
Deduct Standard Power Plant Induced Draft Fans and Ducts	(2,300)	(700)	(2,300)
Deduct Standard Power Plant Electrostatic Precipitator (300°F)	(2,100)	(900)	(2,100)
NET COST INVESTMENT	10,800	3,400	43,400

( ) = Deduction

(a) Costs also include duct insulation.
(b) Cost is for sulfuric acid storage only.
(c) Cost includes V_2O_5 catalyst.

BLE 3

OL PROCESSES
BREAKDOWN

are in M$)

te	Potassium Formate	Ammonia Scrubbing (Base)	Ammonia Scrubbing (A) (Steam Stripping)	Ammonia Scrubbing (B) (Thermal Decomposition)	Tyco	Magnesium Oxide Scrubbing	Zinc Oxide	Citrate
	11,329	5,436	5,997	8,093	9,754	8,422	7,734	6,423
	120	89	282	85	6,949 (d)	1,665	389	4,599
a)	1,106	936	936	936	811	1,182	1,106	1,322
	3,145	1,418	1,689	2,066	2,360	2,173	1,939	2,255
	475	247	258	342	410	470	370	360
	552	160	265	440	290	290	420	360
	16,727	8,286	9,427	11,962	20,574	14,202	11,958	15,319
	13,173	6,314	7,473	9,638	10,226	11,398	9,542	10,281
	6,700							
	36,600	14,600	16,900	21,600	30,800	25,600	21,500	25,600
	2,700							
			3,700	4,400	1,300 (b)	5,600	4,700	
(f)		28,000						
)	(2,300)	(2,300)	(2,300)	(2,300)	(2,300)	(2,300)	(2,300)	(2,300)
)	(2,100)	(2,100)	(2,100)	(2,100)	0	(2,100)	(2,100)	(2,100)
	34,900	38,200	16,200	21,600	29,800	26,800	21,800	21,200

(d) Cost includes nitric acid storage
(e) 300°F Electrostatic Precipitator
(f) 900°F Electrostatic Precipitator

B

TABLE 4

Process	Major Assumptions	Major Changes to Process
Wet Limestone Scrubbing	Basis: TVA 1969 Conceptual Design •Limestone @ 110% stoichiometry •250°F gas reheat required •3-stage UOP TCA scrubber vessel •100% calcination of limestone and 25% conversion of CaO in boiler •90% SO_2 removal •99+% solids removal •12% solids slurry to disposal pond •No deleterious effect on boiler operability from limestone injection •No plugging problems in slurry circuit	•Scaled from 200 to 1000 MW, heat, material balances, ΔP changed as needed •Higher ΔP in reheat system •Increased liquid circulation rate in scrubbers and added 1 extra stage of contact •Recycle waste disposal pond overflow liquid back to process
Dry Limestone Injection	Basis: TVA 1968 Conceptual Design •350 MW maximum size boiler than can be used •200% stoichiometric limestone addition •50% SO_2 removal (25% conversion of CaO) •No deleterious effects on boiler operability •Stack emission particulate level of 0.1 gr/SCF	•Heat, material balances, ΔP changed to reflect MWK bases •Increased grinding from 70%-200 mesh to 99%-325 mesh •15.2% ash in coal vs TVA's 12.0 •Increased size of electrostatic precipitator from TVA's 2.8 to 3.1-fold over standard power plant also increased efficiency from 96.1% to 97.4%

TABLE 4 (Cont'd)

Process	Major Assumptions	Major Changes to Process
Cat-Ox	Basis: SRI Report, Contract CPA22-69-78 •Converter temperature - 900°F •SO_2 conversion - 90% •Flue gas from absorber - 225°F •Product acid strength - 78% •Maximum available size Teflon T.M. exchanger used in acid cooling system is 8"Ø x 13' •Catalyst removal, cleaning and re-charging facilities are "black box" items •Electrostatic precipitators available for 900°F service @ 99.5% efficiency •Product acid storage capacity for 30 days production	•Heat, material balances, ΔP changed as needed to reflect MWK bases •Equipment sized to reflect MWK bases
Molten Carbonate	Basis: Singmaster & Breyer Design, Atomics International reports containing exploratory data •Electrostatic precipitator available with efficiency of 99.5% @ 850°F •0.03% Cl in coal •95% SO_2 removal •95% reduction of M_2SO_4 by carbon •Reducer effluent melt can be filtered to remove solids •88% recovery of lithium salts contained in fly ash and coke filter cakes •No recovery of sodium and potassium salts from filter cakes •92% recovery of sulfur in Claus plant	•Material and heat balances scaled to reflect MWK bases •Gas velocity in absorber reduced from 25 to 10 ft/sec. (8 spray towers instead of 4) •Claus plant feed prequenched

TABLE 4 (Cont'd)

Process	Major Assumptions	Major Changes to Process
Molten Carbonate (Cont'd)	•Assume reducers will work as shown: two compartment vessels, oxidation and reduction zones separated by bridge wall with melt circulating between zones, 3 ft/sec gas velocity, 20 min. liquid holdup •Claus plant off-gas recycled to absorbers •Make-up carbonates are anhydrous •No plugging of spray nozzles by fly ash •Demisters will perform satisfactorily •Suitable materials of construction are available •Carryover of salts into flue gas stream can be reduced to practical level	
Potassium Formate	Basis: ACS paper presented at 1970 meeting in Houston •80% fly ash removed in cyclones •0 back pressure of SO_2 in formate solution •90% SO_2 removal •Absorber is 3-stage spray tower •Absorbers are in heat balance - no enthalpy data available •Fly ash escaping cyclones removed in scrubbers and separated for disposal in centrifuges •Stripper in heat balance - no enthalpy data available •97.5% recovery of sulfur in Claus •O_2 used in Claus instead of air •Natural gas- CO_2 reforming used to generate CO •"Black box" processing step used to recover potassium CO_2 scrubber liquids	•Residence time in regenerator lowered from 2 hrs to 25 min. •Total pressure in regenerator increased from 700 psi to 2000 psi to maintain same CO partial pressure a in ACS paper •Detailed flow sheet not given in input data - MWK design developed from the data given. Supplemented as required by judgment factors and assumptions - see discussion in Appendix for details

TABLE 4 (Cont'd)

Process	Major Assumptions	Major Changes to Process
Ammonia Scrubbing (Base Case - Fertilizer Production)	Basis: TVA 1970 Conceptual Design •90% SO_2 removal •4-stage sieve tray (Impinjet) scrubbers •Oxidation of sulfite and bisulfite takes place in separate vessel •No fly ash removal upstream of scrubbers, 99.5% in scrubbers •Scrubber effluent is 50 wt. % salt solution •Ammonium sulfate solution produced and fed to fertilizer plant •Standard fertilizer plant, $CaSO_4$ waste disposed of as 20% slurry	•Scaled heat, material balances, ΔP, to reflect MWK design conditions (size, coal, etc)
Ammonia Scrubbing (Case A - Steam Stripping Regeneration)	Basis: Same as Base Case plus additional data from TVA's pilot plant; also literature data •Packed column under vacuum used to regenerate scrubber effluent with steam-heated thermosiphon reboiler •68.8% recovery of sulfur removed from flue gas •90% SO_2 removal from flue gas •15% of sulfur absorbed makes sulfate •5/1 sulfate/sulfite-bisulfite ratio used •Weak SO_2-water solution condensed from stripper overhead vapors air-stripped to improve SO_2 recovery	•Flow Sheet heat, material balances, ΔP, equipment selection/design largely by MWK since no detailed process design available
Ammonia Scrubbing (Case B - Thermal Decomposition Regeneration)	Basis: Same as Base Case and Alt. A •90% SO_2 removed from flue gas •83.7% sulfur removed from flue gas is recovered •Effluent S/NH_3 mole ratio, S/C, = 0.85 •80% conversion $(NH_4)_2SO_4$ in elec. furnace •1.25 x stoichiometric $CaCO_3$ used in sulfate reactor •Utilities consumption - 0.2# Steam/# $(NH_4)_2SO_4$ in feed and 350 kwh/ton $(NH_4)_2SO_4$ in feed	•Same as Alternate A above

TABLE 4 (Cont'd)

Process	Major Assumptions	Major Changes to Process
TYCO	Basis: TVA Conceptual Design & Cost Study (Preliminary), A.M. Kinney, Inc. Report, Tyco Final Report •80% NO_x, 90% SO_x removed •Filtering system for removing fly ash from H_2SO_4 stream is "black box" item •Plug flow conditions in SO_2-oxidizer-reactor, with 15 sec. residence time (direct scale-up from bench scale) •Same height of packing in N_2O_3 scrubber as indicated by extrapolating miniplant data •99% stripping efficiency @ 272°F with 99% of NO_x as NO_2, no N_2O formed •Overhead vapor from stripper contains 10% NO_2 •Flooding characteristics for granular carbon same as for 1/4-inch rings •60% HNO_3 and 80% H_2SO_4 produced as byproducts •0.005 wt. % ash can be filtered from 272°F 80% H_2SO_4 on commercial scale	•Liquid hourly space velocity of 10 vs 1 demonstrated •Oxidizing stripper L/G is 10-fold higher than used in laboratory operation •Stripper gas rate (G) is 10-fold higher than used in laboratory operation
MgO	Basis: Experimental data from Babcock and Wilcox, Report 5153, 1970, and block type flow sheet of a conceptual design •Venturi scrubbers remove 98% of fly ash in flue gas •3-stage TCA scrubbers, 95% SO_2 removal, 0.762 wt. % bisulfite concentration in scrubber outlet slurry •Slurry thickened to 30% solids & centrifuged •Rotary dryers used to dry solids and expel water of hydration •Rotary kiln calciners used to regenerate MgO by reduction with carbon •Acid plant included as part of process •30 days' storage of byproduct acid, 98% H_2SO_4 •$Mg(OH)_2$ losses reduced by converting to soluble sulfate and recovering	No data available on sulfite regeneration--entire system derived by MWK w/o data

TABLE 4 (Cont'd)

Process	Major Assumptions	Major Changes to Process
ZnO	Basis: Final Report by The Envirogenics Co., (Div. of Aerojet General Corp.) for Contract PH 86-68-77, Oct. 1970 •Scaled rates and material balance given in report to MWK size and coal; in some cases, equipment scaled •Absorbers in heat balance, 90% SO_2 removal, 4-stage Impinjet scrubbers used •Sulfite to sulfate ratio = 3/1 •Clarifier scaled from report - no settling data given •Process equipment for formation, crystallization and thickening of $ZnSO_3$ scaled from Envirogenics report •Superdecanting centrifuges are capable of separating $ZnSO_3$ crystals from lean solution of sulfite-bisulfite •All calcined particles are larger than 40 microns •Indirect kilns used to calcine hydrated zinc sulfite •30 days' storage of 98.5% H_2SO_4 byproduct acid provided •Filters on thickened waste slurry (fly ash + $CaSO_4$) sized based on gypsum filtering rates	•Add mechanical separators for fly ash removal •Add H_2SO_4 plant •Substitute grinding mill for hammer mill on dryer effluent solids
Citrate	Basis: Status reports and summaries of laboratory and pilot plant testing by USBM, Jan. 1971; general literature for H_2S production •90% SO_2 removal @ 105°F •Liquid sulfur-fly ash slurry centrifuged to remove fly ash •4.3 gm. SO_2/liter solution, equivalent to about 80% approach to equilibrium	•Higher sodium to citric acid ratio used, 5.3 vs 1.5

TABLE 4 (Cont'd)

Process	Major Assumptions	Major Changes to Process
Citrate (Cont'd)	•Citric acid concentration, 0.87 gm mol/liter •Na/citric acid ratio of 5.3 atoms/mol •100% conversion of SO_2 @ 5% excess H_2S and 10-min. residence time •Extrapolation of absorption data to low concentration of SO_2 (most available data on smelter gas) •Two-step system to produce H_2S: $CH_4 + S \longrightarrow CS_2 + H_2S$, followed by hydrolysis of CS_2 to H_2S	

its dew point, thereby forming H_2SO_4 on the exchanger surface. Although carbon steel has been used in the present estimates, corrosion resistant materials (e.g. Alloy 20) are actually required and this would significantly increase the cost. A new optimization study is required to determine the best method of reheat including several different levels of gas temperature. It is felt, however, that the present allowance for the reheat system investment is adequate even though the method of reheating is still uncertain. As a point of interest, the cost of Alloy 20 exchangers, which was received too late to incorporate in the estimates, would add about $3-4 MM to the present investment.

Some "black box" items were required where process requirements were not sufficiently defined to permit a normal estimate to be made. Specific examples of this is the fly ash filter in the Tyco process and the solution regeneration operation in the Formate process. In the Tyco case, a brief discussion was held with a vendor and a very approximate type investment was obtained for the fly ash filter but additional data are needed to firm up this number. For the Formate solution regeneration operation a purely arbitrary allowance was included. Obviously, additional process definition is required to eliminate the "black box" items from all the flow sheets but the overall effect on process investment should be small.

In those processes which require the use of a very efficient mist eliminator (Tyco, Cat-Ox, Formate), a Brink type has been specified. The vendor for these items was contacted and a price was obtained which supposedly included the containment vessels. After the estimates had been completed, however, the vendor sent a revision which indicated that the original quote did not include the containment vessels. If the cost of these vessels does have to be added then the present estimates will increase by several million dollars. However, since the cost presently included for the Brink mist eliminators is several million dollars, it is likely that some other equally efficient type might be found for this price and the present costs would, therefore, be unchanged. Consequently, the additional cost of the containment vessels was not included in the present estimates. Since mist elimination in these processes is of major importance, extensive experimental data in this area eventually will be required to provide a sound basis for both process design and cost estimating.

Waste disposal is a major problem in some processes, notably those using limestone, both wet scrubbing and dry injection. Since the method of disposal will vary from site to site (e.g., ocean dumping, land fill, removal by outside contractor), it was decided not to attempt to estimate the cost of waste disposal as an investment but rather to include it as an operating cost. Waste disposal would have to be considered in detail, however, for a specific installation, including such factors as potential water pollution.

B. Operating Costs

Operating costs have been calculated in the manner requested by APCO, viz, as mills per kilowatt hour and as dollars per ton of sulfur not emitted, considering both credit and no credit for by-products. A breakdown of these costs for each process studied is given in Tables 6 - 17. Since the individual items shown in the tables are generally self-explanatory, no detailed discussion of these will be given. However, a separate listing, and in some cases a brief rationale, of the specific values used for the various items is included below for convenience.

1. Plant Site Location - Cincinnati, Ohio.

2. Fixed Cost - Annual % of capital investment.

   a. 15-year plant life, sinking fund method with cost of money at 8%; depreciation is 3.68%. Interim replacements of 0.35%; total is 4.03%.

   b. Taxes - Federal tax of 3.61%, local taxes of 2.33%, total is 5.94%; basis FPC Power Supply Area 12.

   c. Insurance - 0.25%.

   The sum of a + b + c is 10.22% which combined with the cost of money at 8% gives a total of 18.22% for fixed charges. Other combinations of plant life and cost of money would, of course, produce other fixed charge rates (e.g., 30-year life and 6% money gives 13.8% while 10-year life and 9% money results in 22.12% charges) but the one selected appears reasonable for the present evaluation.

3. Direct Costs

   a. Labor Rate - $4.50/hour based on U. S. Bureau of Labor statistics for stationary engineers, boiler firemen, and average production worker in the Cincinnati area. Supervision at 15% of labor.

   b. Maintenance - Will vary with the process. A range of 4-5% of capital investment has been specified for the present evaluations with the actual value used based on judgment factors applied to each process.

c. Cost of Raw Materials, Plant Supplies - Plant supplies will be 15% of maintenance costs. A listing of chemical prices is shown in Table 5.

d. Waste Disposal (Excluding Fly Ash) - 50¢/Ton.

e. Utilities

Steam (≈150 psia)	40¢/M Lb
Process Water	20¢/M Gal
Treated Process Water (BFW Quality)	40¢/M Gal
Cooling Water	2.5¢/M Gal
Coal	$8.00/Ton
Fuel Gas	40¢/MM Btu
Electricity	6.75 mills/Kwh

(This electricity cost was derived from coal-fired steam-electric plant production expense data available from the FPC and the National Coal Association for the plant site area. Projected escalation for the 1971 power costs is included.

The value shown is the total production cost and assumes that the power used by the SO_2-control process will cost as much to generate as does power sold to outside customers. An alternative approach would be to consider the power requirements of the SO_2-control process on an incremental basis such that the power cost is equal only to the additional fuel burned. This latter method would produce power costs about one-half those actually used. Since there is not a large difference in the power consumed among the processes studied, it was not considered justified to spend the time needed to prepare a separate study of the proper method of charging power to SO_2- control processes. Therefore, the total production costs were used in the present evaluations.)

TABLE 5

CHEMICAL AND RAW MATERIAL PRICES

Material	Price
Ammonia	$50/Ton (Anhyd.)
Catalysts:	
Activated Carbon	$.38/Lb.
Nitric Acid Catalyst	$120/troy oz.
Sulfuric Acid Catalyst	$1.09/Lb.
Citric Acid	$.30/Lb.
Coal	$8/Ton
Coke (Petroleum)	$8/Ton
Lime	$15/Ton
Limestone	$2/Ton
Lithium Carbonate	$.42/Lb.
Magnesia	$40/Ton
Nitric Acid (60%)	$25/Ton
Oxygen ("over-the-fence")	$12/Ton
Phosphate Rock	$11.88/Ton
Potassium Carbonate	$.05/Lb.
Sodium Carbonate	$.02/Lb.
Sodium Hydroxide	$.03/Lb. (dry)
Zinc Oxide	$.15/Lb.

4. Indirect Costs

a. Payroll Burden - 20% of operating labor and supervision.

b. Plant Overhead - 50% of operating labor, supervision, maintenance, and supplies.

5. By-Product Credit

Sulfuric Acid
98% acid @ $12/short ton of 100% acid.
80% acid @ $ 6/short ton of 100% acid.

Nitric Acid (57-60%) at $25/short ton of 100% acid.

As previously indicated, the power station thermal efficiency used in the present study is about 38% (9,000 Btu/Kwh) and the load factor is about 80% (7,000 hours/year). The same load factor (i.e., 7,000 hours/year) was used for the full fifteen-year assumed life of the SO_2- control plant which differs somewhat from TVA's recommended figures of 7,000 hours/year the first ten years and 5,000 hours/year for the next five. However, since there does not appear to be universal agreement on what load factor should be used for power plants and since the load factor will not have a major influence on the comparisons of the various SO_2- control processes studied, use of an 80% load factor appears reasonable.

TABLE 6

ANNUAL OPERATING COSTS
WET LIMESTONE SCRUBBING

Plant Size (MW)		1000
Fixed Capital Investment (FCI)	-	$10,800,000
Stream Time (hrs/yr)		7000

	DIRECT COST	$/YEAR
1.	Operating Labor (2 men/shift @ $4.50/hr)	78,840
2.	Supervision - 15% of Item 1	11,830
3.	Maintenance Labor and Materials - 4% of FCI	432,000
4.	Plant Supplies - 15% of Item 3	64,800
5.	Utilities	
	A. Cooling Water - — GPM at $.025/M gal	—
	B. Process Water - — GPM at $.20/M gal	—
	C. Electric Power - 25,310 KW at 6.75 mills/KWH	1,195,860
	D. Natural Gas - — MSCFH at $.40/MSCF	—
	E. Steam - — M lbs/hr at $.45/M lbs	—
6.	Chemicals and Raw Materials	
	A. Limestone - 1,237 TPD @ $2/TON	721,700
	B. Extra Coal* - 3 TPH @ $8/TON	168,000
6a.	Solids Disposal (ex fly ash) - 57 TPH @ $.50/TON	199,500
7.	Subtotal Direct Cost (ex credits)	$ 2,872,530
8.	Credits	
	None	—
9.	Total Direct Cost	$ 2,872,530
	INDIRECT COST	
10.	Payroll Overhead - 20% of (1+2)	18,130
11.	Plant Overhead - 50% of (1+2+3+4)	293,740
12.	Total Indirect Cost	$ 301,870
	FIXED COST	
13.	Capital Charges - 18.22% of FCI (Includes Depreciation, Interim Replacements, Insurance, Taxes, and Cost of Capital)	$ 1,967,760
	TOTAL OPERATING COST	
14.	Net Production Cost - Items (9+12+13)	$ 5,142,160
	UNIT PRODUCTION COST	
15.	Gross - Items (7+12+13)	$ 5,142,160
	A. Mills/KWH	.73
	B. $/Ton S not emitted	65.2
16.	Net - Items (9+12+13)	$ 5,142,160
	A. Mills/KWH	.73
	B. $/Ton S not emitted	65.2

* Extra coal needed for limestone calcination in boiler

TABLE 7

ANNUAL OPERATING COSTS
DRY LIMESTONE INJECTION

Plant Size (MW)		350
Fixed Capital Investment (FCI)	-	$3,400,000
Stream Time (hrs/yr)		7000

	DIRECT COST	$/YEAR
1.	Operating Labor (1 man/shift @ $4.50/hr)	39,420
2.	Supervision - 15% of Item 1	5,910
3.	Maintenance Labor and Materials - 4% of FCI	136,000
4.	Plant Supplies - 15% of Item 3	20,400
5.	Utilities	
	A. Cooling Water - — GPM at $.025/M gal	—
	B. Process Water - — GPM at $.20/M gal	—
	C. Electric Power - 4,420 KW at 6.75 mills/KWH	208,850
	D. Natural Gas - — MSCFH at $.40/MSCF	—
	E. Steam - — M lbs/hr at $.45/M lbs	—
6.	Chemicals and Raw Materials	
	A. Limestone - 716 TPD @ $2/TON	417,700
	B. Extra Coal* - 1.05 TPH @ $8/TON	58,800
6a.	Solids Disposal (ex fly ash) - 29 TPH @ $.50/TON	101,500
7.	Subtotal Direct Cost (ex credits)	$ 988,580
8.	Credits	
	None	—
9.	Total Direct Cost	$ 988,580
	INDIRECT COST	
10.	Payroll Overhead - 20% of (1+2)	9,070
11.	Plant Overhead - 50% of (1+2+3+4)	100,870
12.	Total Indirect Cost	$ 109,940
	FIXED COST	
13.	Capital Charges - 18.22% of FCI (Includes Depreciation, Interim Replacements, Insurance, Taxes, and Cost of Capital)	$ 619,480
	TOTAL OPERATING COST	
14.	Net Production Cost - Items (9+12+13)	$ 1,717,800
	UNIT PRODUCTION COST	
15.	Gross - Items (7+12+13)	$ 1,718,000
	A. Mills/KWH	.70
	B. $/Ton S not emitted	112.2
16.	Net - Items (9+12+13)	$ 1,718,000
	A. Mills/KWH	.70
	B. $/Ton S not emitted	112.2

* Extra coal needed for limestone calcination in boiler

TABLE 8

ANNUAL OPERATING COSTS
CAT-OX

Plant Size (MW)		1000
Fixed Capital Investment (FCI)	-	$43,400,000
Stream Time (hrs/yr)		7000

		$/YEAR
	DIRECT COST	
1.	Operating Labor (4 men/shift @ $4.50/hr)	157,680
2.	Supervision - 15% of Item 1	23,650
3.	Maintenance Labor and Materials - 4.5% of FCI	1,953,000
4.	Plant Supplies - 15% of Item 3	292,950
5.	Utilities	
	A. Cooling Water - 548 GPM at $.025/M gal	5,760
	B. Process Water - — GPM at $.20/M gal	—
	C. Electric Power - 17,800 KW at 6.75 mills/KWH	841,050
	D. Natural Gas - — MSCFH at $.40/MSCF	—
	E. Steam - — M lbs/hr at $.45/M lbs	—
6.	Chemicals and Raw Materials	
	A. Sulfuric Acid Catalyst - 1330 ft^3/yr @ $38.23/ft^3	50,850
7.	Subtotal Direct Cost (ex credits)	$ 3,324,940
8.	Credits	
	A. Sulfuric Acid (78%) - 1061 TPD @ $6/TON 100%	(1,447,250)
	B. Stack Gas Cooling* - 162 MM Btu/hr @ $.40/MM Btu/hr	(453,600)
9.	Total Direct Cost	$ 1,424,090
	INDIRECT COST	
10.	Payroll Overhead - 20% of (1+2)	36,270
11.	Plant Overhead - 50% of (1+2+3+4)	1,213,640
12.	Total Indirect Cost	$ 1,249,910
	FIXED COST	
13.	Capital Charges - 18.22% of FCI (Includes Depreciation, Interim Replacements, Insurance, Taxes, and Cost of Capital)	$ 7,907,480
	TOTAL OPERATING COST	
14.	Net Production Cost - Items (9+12+13)	$10,581,460
	UNIT PRODUCTION COST	
15.	Gross - Items (7+12+13)	$12,482,330
	A. Mills/KWH	1.78
	B. $/Ton S not emitted	158.0
16.	Net - Items (9+12+13)	$10,581,460
	A. Mills/KWH	1.51
	B. $/Ton S not emitted	133.9

* Credit for stack gas at 225°F vs base case 300°F

TABLE 9

ANNUAL OPERATING COSTS
MOLTEN SALT

Plant Size (MW)	1000
Fixed Capital Investment (FCI) -	$34,600,000
Stream Time (hrs/yr)	7000

	DIRECT COST	$/YEAR
1.	Operating Labor (5 men/shift @ $4.50/hr)	197,100
2.	Supervision - 15% of Item 1	29,570
3.	Maintenance Labor and Materials - 5% of FCI	1,730,000
4.	Plant Supplies - 15% of Item 3	259,500
5.	Utilities	
	A. Cooling Water - 650 GPM at $.025/M gal	6,830
	B. Process Water - — GPM at $.20/M gal	—
	C. Electric Power - 14,575 KW at 6.75 mills/KWH	688,670
	D. Natural Gas - — MSCFH at $.40/MSCF	—
	E. Steam - — M lbs/hr at $.45/M lbs	—
6.	Chemicals and Raw Materials	
	A. Lithium Carbonate - 115 lbs/hr @ $.42/lb	338,100
	B. Sodium Carbonate - 990 lbs/hr @ $.02/lb	138,600
	C. Potassium Carbonate - 1684 lbs/hr @ $.05/lb	589,400
	D. Petroleum Coke - 15.75 TPH @ $8/TON	882,000
6a.	Solids Disposal (ex fly ash) - 1 TPH @ $.50/TON	3,500
7.	Subtotal Direct Cost (ex credits)	$ 4,863,270
8.	Credits	
	A. Sulfur - 261 TPD @ $20/Short Ton	(1,522,500)
9.	Total Direct Cost	$ 3,340,770
	INDIRECT COST	
10.	Payroll Overhead - 20% of (1+2)	45,330
11.	Plant Overhead - 50% of (1+2+3+4)	1,108,090
12.	Total Indirect Cost	$ 1,153,420
	FIXED COST	
13.	Capital Charges - 18.22% of FCI (Includes Depreciation, Interim Replacements, Insurance, Taxes, and Cost of Capital)	$ 6,304,120
	TOTAL OPERATING COST	
14.	Net Production Cost - Items (9+12+13)	$10,798,310
	UNIT PRODUCTION COST	
15.	Gross - Items (7+12+13)	$12,320,910
	A. Mills/KWH	1.76
	B. $/Ton S not emitted	148.4
16.	Net - Items (9+12+13)	$10,798,310
	A. Mills/KWH	1.54
	B. $/Ton S not emitted	130.1

TABLE 10

ANNUAL OPERATING COSTS
POTASSIUM FORMATE

Plant Size (MW)	1000
Fixed Capital Investment (FCI) -	$34,900,000
Stream Time (hrs/yr)	7000

DIRECT COST	$/YEAR
1. Operating Labor (4 men/shift @ $4.50/hr)	157,680
2. Supervision - 15% of Item 1	23,650
3. Maintenance Labor and Materials - 4.5% of FCI	1,570,500
4. Plant Supplies - 15% of Item 3	235,580
5. Utilities	
A. Cooling Water - 30,000 GPM at $.025/M gal	315,000
B. Process Water - 1,840 GPM at $.20/M gal	154,560
C. Electric Power - 37,540 KW at 6.75 mills/KWH	1,680,890
D. Natural Gas - 553 MSCFH at $.40/MSCF	1,548,800
E. Steam - 116 M lbs/hr at $.45/M lbs	157,500
6. Chemicals and Raw Materials	
A. Potassium Carbonate - 250 lbs/hr @ $.05/lb	87,500
7. Subtotal Direct Cost (ex credits)	$ 5,931,660
8. Credits	
A. Sulfur - 245 TPD @ $20/Short Ton	(1,429,200)
9. Total Direct Cost	$ 4,502,460
INDIRECT COST	
10. Payroll Overhead - 20% of (1+2)	36,270
11. Plant Overhead - 50% of (1+2+3+4)	993,710
12. Total Indirect Cost	$ 1,029,980
FIXED COST	
13. Capital Charges - 18.22% of FCI (Includes Depreciation, Interim Replacements, Insurance, Taxes, and Cost of Capital)	$ 6,358,780
TOTAL OPERATING COST	
14. Net Production Cost - Items (9+12+13)	$11,891,220
UNIT PRODUCTION COST	
15. Gross - Items (7+12+13)	$13,320,420
A. Mills/KWH	1.90
B. $/Ton S not emitted	169.3
16. Net - Items (9+12+13)	$11,891,220
A. Mills/KWH	1.70
B. $/Ton S not emitted	150.7

TABLE 11A

ANNUAL OPERATING COSTS
AMMONIA SCRUBBING (BASE)
$(NH_4)_2\ SO_4$ PRODUCTION
(324,800 TPY)

Plant Size (MW) 1000
Fixed Capital Investment (FCI) - $ 10,200,000
Stream Time (hrs/yr) 7000

DIRECT COST	$/YEAR
1. Operating Labor (3 men/shift @ $4.50/hr)	118,260
2. Supervision - 15% of Item 1	17,740
3. Maintenance Labor and Materials - 4.5% of FCI	459,000
4. Plant Supplies - 15% of Item 3	68,850
5. Utilities	
A. Cooling Water - 8,800 GPM at $.025/M gal	92,400
B. Process Water - 5,000 GPM at $.20/M gal	420,000
C. Electric Power - 24,647 KW at 6.75 mills/KWH	1,164,600
D. Natural Gas - — MSCFH at $.40/MSCF	—
E. Steam - 390 M lbs/hr at $.45/M lbs	1,228,500
6. Chemicals and Raw Materials	
A. Ammonia - 287 TPD @ $50/TON	4,190,200
7. Subtotal Direct Cost (ex credits)	$7,759,550
8. Credits	
9. Total Direct Cost	
INDIRECT COST	
10. Payroll Overhead - 20% of (1+2)	27,200
11. Plant Overhead - 50% of (1+2+3+4)	331,930
12. Total Indirect Cost	$ 359,130
FIXED COST	
13. Capital Charges - 18.22% of FCI (Includes Depreciation, Interim Replacements, Insurance, Taxes, and Cost of Capital)	$1,858,440
TOTAL OPERATING COST	
14. Net Production Cost - Items (9+12+13)	$9,977,120
UNIT PRODUCTION COST	
15. Gross - Items (7+12+13)	$9,977,120
A. Mills/KWH	1.43
B. $/Ton S not emitted	126.8
C. $/Ton $(NH_4)_2\ SO_4$	30.80

TABLE 11B

ANNUAL OPERATING COSTS
AMMONIA SCRUBBING (BASE)
HNO_3/FERTILIZER PRODUCTION
(691,250 TPY FERTILIZER)

Plant Size (MW) - 1000
Fixed Capital Investment (FCI) - $28,000,000
Stream Time (hrs/yr) - 7000

			$/YEAR
DIRECT COST			
1. Operating Labor (14 men/shift @ $4.50/hr)			551,880
2. Supervision - 15% of Item 1			82,780
3. Maintenance Labor and Materials - 4.5% of FCI			1,260,000
4. Plant Supplies - 15% of Item 3			189,000
5. Utilities			
A. Cooling Water	- —	GPM at $.025/M gal	—
B. Process Water	- 25,000*	GPM at $.40/M gal	4,200,000
C. Electric Power	- 6,135	KW at 6.75 mills/KWH	289,900
D. Natural Gas	- —	MSCFH at $.40/MSCF	—
E. Steam	- 398	M lbs/hr at $.45/M lbs	1,253,700
6. Chemicals and Raw Materials			
A. $(NH_4)_2SO_4$ Transfer Price	- 1112	TPD @ $30.80/TON	10,800,880
B. Ammonia	- 517	TPD @ $50/TON	7,548,200
C. Phosphate Rock	- 1128	TPD @ $11.88/TON	3,908,500
D. Anti-Foam Agent	- 900	lbs/day @ $.15/lb	39,420
E. Nitric Acid Cat	- 119.4	tr.oz @ $120/oz	14,330
F. Conditioner	- 48	TPD @ $46.6/TON	653,150
6a. Solids Disposal	- 72	TPH @ $.50/TON	252,000
7. Subtotal Direct Cost (ex credits)			$30,243,740
8. Credits			—
9. Total Direct Cost			$ —
INDIRECT COST			
10. Payroll Overhead - 20% of (1+2)			126,930
11. Plant Overhead - 50% of (1+2+3+4)			1,041,830
12. Total Indirect Cost			$ 1,168,760
FIXED COST			
13. Capital Charges - 18.22% of FCI (Includes Depreciation, Interim Replacements, Insurance, Taxes, and Cost of Capital)			$ 5,101,600
TOTAL OPERATING COST			
14. Net Production Cost - Items (9+12+13)			$36,514,100
UNIT PRODUCTION COST			
15. Gross - Items (7+12+13)			$36,514,100
A. $/Ton Fertilizer			$ 52.82
B. $/Ton Fertilizer w. Ammonia @ $30/TON			$ 46.03

* Chloride free water of BFW quality @ $.40/M gal

TABLE 12

ANNUAL OPERATING COSTS
AMMONIA SCRUBBING (A)
(STEAM STRIPPING)

Plant Size (MW) 1000
Fixed Capital Investment (FCI) - $16,200,000
Stream Time (hrs/yr) 7000

DIRECT COST	$/YEAR
1. Operating Labor (4 men/shift @ $4.50/hr)	157,680
2. Supervision - 15% of Item 1	23,650
3. Maintenance Labor and Materials - 4.5% of FCI	729,000
4. Plant Supplies - 15% of Item 3	109,350
5. Utilities	
A. Cooling Water - 24,640 GPM at $.025/M gal	258,830
B. Process Water - 3,000 GPM at $.20/M gal	252,000
C. Electric Power - 18,298 KW at 6.75 mills/KWH	864,000
D. Natural Gas - — MSCFH at $.40/MSCF	—
E. Steam - 500 M lbs/hr at $.45/M lbs	1,575,000
6. Chemicals and Raw Materials	
A. Limestone - 250 TPD @ $2/TON	291,700
B. Ammonia - 300 lbs/hr @ $50/TON	52,500
6a. Solids Disposal (ex fly ash) - 13.3 TPH @ $.50/TON	46,550
7. Subtotal Direct Cost (ex credits)	$ 4,360,860
8. Credits	
A. Sulfuric Acid (98.5%) - 570 TPD @ $12/TON	(1,995,000)
9. Total Direct Cost	$ 2,365,860
INDIRECT COST	
10. Payroll Overhead - 20% of (1+2)	36,270
11. Plant Overhead - 50% of (1+2+3+4)	509,850
12. Total Indirect Cost	$ 546,120
FIXED COST	
13. Capital Charges - 18.22% of FCI (Includes Depreciation, Interim Replacements, Insurance, Taxes, and Cost of Capital)	$ 2,951,640
TOTAL OPERATING COST	
14. Net Production Cost - Items (9+12+13)	$ 5,863,620
UNIT PRODUCTION COST	
15. Gross - Items (7+12+13)	$ 7,858,620
A. Mills/KWH	1.12
B. $/Ton S not emitted	99.88
16. Net - Items (9+12+13)	$ 5,863,620
A. Mills/KWH	0.84
B. $/Ton S not emitted	74.25

TABLE 13

ANNUAL OPERATING COSTS
AMMONIA SCRUBBING (B)
(THERMAL DECOMPOSITION)

Plant Size (MW)	1000
Fixed Capital Investment (FCI) -	$21,600,000
Stream Time (hrs/yr)	7000

		$/YEAR
DIRECT COST		
1.	Operating Labor (4 men/shift @ $4.50/hr)	157,680
2.	Supervision - 15% of Item 1	23,650
3.	Maintenance Labor and Materials - 4.5% of FCI	972,000
4.	Plant Supplies - 15% of Item 3	145,800
5.	Utilities	
	A. Cooling Water - 8,000 GPM at $.025/M gal	84,000
	B. Process Water - 400 GPM at $.20/M gal	33,600
	C. Electric Power - 40,218 KW at 6.75 mills/KWH	1,900,300
	D. Natural Gas -- — MSCFH at $.40/MSCF	—
	E. Steam * - 76.9 M lbs/hr at $.45/M lbs	260,160
6.	Chemicals and Raw Materials	
	A. Ammonia - 300 lbs/hr @ $50/TON	52,500
	B. Limestone - 168 TPD @ $2/TON	98,000
6a.	Solids Disposal (ex fly ash) - 9 TPH @ $.50/TON	31,500
7.	Subtotal Direct Cost (ex credits)	$ 3,759,190
8.	Credits	
	A. Sulfuric Acid (98.5%) - 692 TPD @ $12/TON	(2,422,000)
9.	Total Direct Cost	$ 1,337,190
INDIRECT COST		
10.	Payroll Overhead - 20% of (1+2)	36,270
11.	Plant Overhead - 50% of (1+2+3+4)	649,570
12.	Total Indirect Cost	$ 685,840
FIXED COST		
13.	Capital Charges - 18.22% of FCI (Includes Depreciation, Interim Replacements, Insurance, Taxes, and Cost of Capital)	$ 3,935,520
TOTAL OPERATING COST		
14.	Net Production Cost - Items (9+12+13)	$ 5,958,550
UNIT PRODUCTION COST		
15.	Gross - Items (7+12+13)	$ 8,380,550
	A. Mills/KWH	1.20
	B. $/Ton S not emitted	106.6
16.	Net - Items (9+12+13)	$ 5,958,550
	A. Mills/KWH	.85
	B. $/Ton S not emitted	75.5

* 51,300 lbs/hr (150 psia) @ $.45/M lbs
25,600 lbs/hr (700°F superheated) @ $.55/lb

TABLE 14

ANNUAL OPERATING COSTS
TYCO

Plant Size (MW) 1000
Fixed Capital Investment (FCI) - $29,800,000
Stream Time (hrs/yr) 7000

		$/YEAR
DIRECT COST		
1.	Operating Labor (5 men/shift @ $4.50/hr)	197,100
2.	Supervision - 15% of Item 1	29,570
3.	Maintenance Labor and Materials - 5% of FCI	1,490,000
4.	Plant Supplies - 15% of Item 3	223,500
5.	Utilities	
	A. Cooling Water - 1,720 GPM at $.025/M gal	18,060
	B. Process Water - 8 GPM at $.20/M gal	1,340
	C. Electric Power - 24,730 KW at 6.75 mills/KWH	1,168,480
	D. Natural Gas - — MSCFH at $.40/MSCF	—
	E. Steam - — M lbs/hr at $.45/M lbs	—
6.	Chemicals and Raw Materials	
	A. Activated Carbon* - 68,000 ft³/year @ $13.50/ft³	918,000
	B. Limestone - 1.25 TPH @ $2/TON	17,500
6a.	Solids Disposal (ex fly ash) - 1 TPH @ $.50/TON	3,500
7.	Subtotal Direct Cost (ex credits)	$ 4,067,050
8.	Credits	
	A. Sulfuric Acid (80%) - 971 TPD @ $6/TON 100%	(1,359,500)
	B. Nitric Acid (60%) - 14[illegible] TPD @ $25/TON 100%	(648,000)
	C. BFW Heating - 170 MM Btu/hr @ $.40/MM Btu	(474,900)
9.	Total Direct Cost	$ 1,584,650
INDIRECT COST		
10.	Payroll Overhead - 20% of (1+2)	45,330
11.	Plant Overhead - 50% of (1+2+3+4)	970,090
12.	Total Indirect Cost	$ 1,015,420
FIXED COST		
13.	Capital Charges - 18.22% of FCI (Includes Depreciation, Interim Replacements, Insurance, Taxes, and Cost of Capital)	$ 5,429,560
TOTAL OPERATING COST		
14.	Net Production Cost - Items (9+12+13)	$ 8,029,630
UNIT PRODUCTION COST		
15.	Gross - Items (7+12+13)	$10,512,030
	A. Mills/KWH	1.50
	B. $/Ton S not emitted	137.7
16.	Net - Items (9+12+13)	$ 8,029,630
	A. Mills/KWH	1.15
	B. $/Ton S not emitted	104.7

* Assume one year activated carbon life in catalytic stripper.

TABLE 15

ANNUAL OPERATING COSTS
MAGNESIUM OXIDE SCRUBBING

Plant Size (MW)	1000
Fixed Capital Investment (FCI)	$26,800,000
Stream Time (hrs/yr)	7000

DIRECT COST		$/YEAR
1.	Operating Labor (4 men/shift @ $4.50/hr)	157,680
2.	Supervision - 15% of Item 1	23,650
3.	Maintenance Labor and Materials - 4% of FCI	1,072,000
4.	Plant Supplies - 15% of Item 3	160,800
5.	Utilities	
	A. Cooling Water - 4,230 GPM @ $.025/M gal	44,420
	B. Process Water - 616 GPM @ $.20/M gal	51,740
	C. Electric Power - 22,656 KW @ 6.75 mills/KWH	1,070,500
	D. Natural Gas - 268 MSCFH @ $.40/MSCF	750,400
	E. Steam - —— M lbs/hr @ $.45/M lbs	--
6.	Chemicals and Raw Materials	
	A. Magnesia - 5 TPD @ $40/TON	58,330
	B. Petroleum Coke - 645 lbs/hr (dry) @ $8/TON	18,060
	C. Limestone - 1,500 lbs/hr @ $2/TON	10,500
7.	Subtotal Direct Cost (ex credits)	$3,418,080
8.	Credits	
	A. Sulfuric Acid (98.5%) - 890 TPD	(3,115,000)
9.	Total Direct Cost	$ 303,080
INDIRECT COST		
10.	Payroll Overhead - 20% of (1+2)	36,270
11.	Plant Overhead - 50% of (1+2+3+4)	707,070
12.	Total Indirect Cost	$743,340
FIXED COST		
13.	Capital Charges - 18.22% of FCI (Includes Depreciation, Interim Replacements, Insurance, Taxes, and Cost of Capital)	$4,882,960
TOTAL OPERATING COST		
14.	Net Production Cost - Items (9+12+13)	$5,929,380
UNIT PRODUCTION COST		
15.	Gross - Items (7+12+13)	$9,044,380
	A. Mills/KWH	1.29
	B. $/Ton S not emitted	111.1
16.	Net - Items (9+12+13)	$5,929,380
	A. Mills/KWH	0.85
	B. $/Ton S not emitted	71.3

TABLE 16

ANNUAL OPERATING COSTS
ZINC OXIDE SCRUBBING

Plant Size (MW)	1000
Fixed Capital Investment (FCI)	$21,800,000
Stream Time (hrs/yr)	7000

DIRECT COST		$/YEAR
1.	Operating Labor (4 men/shift @ $4.50/hr)	157,680
2.	Supervision - 15% of Item 1	23,650
3.	Maintenance Labor and Materials - 4% of FCI	872,000
4.	Plant Supplies - 15% of Item 3	130,800
5.	Utilities	
	A. Cooling Water - 5,320 GPM @ $.025/M gal	55,860
	B. Process Water - 47 GPM @ $.20/M gal	4,000
	C. Electric Power - 20,130 KW @ 6.75 mills/KWH	951,140
	D. Natural Gas - 145.3 MSCFH @ $.40/MSCF	406,840
	E. Steam - —— M lbs/hr @ $.45/M lbs	—
6.	Chemicals and Raw Materials	
	A. Zinc Oxide - 200 lbs/hr @ $.15/lb	210,000
	B. Sodium Carbonate - 325 lbs/hr @ $.02/lb	45,500
	C. Lime - 2.1 TPH @ $15/TON	220,500
6a.	Solids Disposal (ex fly ash) - 14.2 TPH @ $.50/TON	49,700
7.	Subtotal Direct Cost (ex credits)	$3,127,670
8.	Credits	
	A. Sulfuric Acid (98.5%) - 754 TPD @ $12/TON	(2,639,000)
9.	Total Direct Cost	$ 488,670
INDIRECT COST		
10.	Payroll Overhead - 20% of (1+2)	36,270
11.	Plant Overhead - 50% of (1+2+3+4)	592,070
12.	Total Indirect Cost	$ 628,340
FIXED COST		
13.	Capital Charges - 18.22% of FCI (Includes Depreciation, Interim Replacements, Insurance, Taxes, and Cost of Capital)	$3,971,960
TOTAL OPERATING COST		
14.	Net Production Cost - Items (9+12+13)	$5,088,970
UNIT PRODUCTION COST		
15.	Gross - Items (7+12+13)	$7,727,970
	A. Mills/KWH	1.10
	B. $/Ton S not emitted	98.1
16.	Net - Items (9+12+13)	$5,088,970
	A. Mills/KWH	0.73
	B. $/Ton S not emitted	64.4

TABLE 17

ANNUAL OPERATING COSTS
CITRATE

Plant Size (MW) 1000
Fixed Capital Investment (FCI) - $21,200,000
Stream Time (hrs/yr) 7000

DIRECT COST	$/YEAR
1. Operating Labor (4 men/shift @ $4.50/hr)	157,680
2. Supervision - 15% of Item 1	23,650
3. Maintenance Labor and Materials - 4% of FCI	848,000
4. Plant Supplies - 15% of Item 3	127,200
5. Utilities	
A. Cooling Water - 34,395 GPM at $.025/M gal	361,150
B. Process Water - 537 GPM at $.20/M gal	45,100
C. Electric Power - 18,550 KW at 6.75 mills/KWH	920,000
D. Natural Gas - 171.4 MSCFH at $.40/MSCF	479,900
E. Steam - 25 M lbs/hr at $.45/M lbs	78,950
6. Chemicals and Raw Materials	
A. Na_2CO_3 - 135 lbs/hr @ $.02/lb	18,900
B. Citric Acid - 92 lbs/hr @ $.30/lb	193,200
C. Limestone - 24.5 TPD @ $2/TON	14,300
6a. Solids Disposal (ex fly ash) - 1.5 TPH @ $.50/TON	5,250
7. Subtotal Direct Cost (ex credits)	$ 3,273,280
8. Credits	
A. Sulfur - 251 TPD @ $20/Short TON	(1,464,170)
9. Total Direct Cost	$ 1,809,110
INDIRECT COST	
10. Payroll Overhead - 20% of (1+2)	36,270
11. Plant Overhead - 50% of (1+2+3+4)	578,280
12. Total Indirect Cost	$ 615,050
FIXED COST	
13. Capital Charges - 18.22% of FCI (Includes Depreciation, Interim Replacements, Insurance, Taxes, and Cost of Capital)	$ 3,862,640
TOTAL OPERATING COST	
14. Net Production Cost - Items (9+12+13)	$ 6,286,800
UNIT PRODUCTION COST	
15. Gross - Items (7+12+13)	$ 7,750,970
A. Mills/KWH	1.11
B. $/Ton S not emitted	98.3
16. Net - Items (9+12+13)	$ 6,286,800
A. Mills/KWH	0.90
B. $/Ton S not emitted	79.4

VI. IMPACT

The potential SO_2 emission (without abatement) from power plants burning coal and oil has been estimated as follows (Reference 1):

	SO_2 Emission, Millions of Tons/Year						
	1970	1975	1980	1990	2000	2010	2020
Power Plants	20.0	30.2	41.1	62.0	94.5	116	88
All Other	16.6	18.0	19.8	24.4	31.3	-	-
TOTAL	36.6	48.2	60.9	86.4	125.8	-	-

The use of coal will continue to increase and will approximately triple by the year 2000. Peak SO_2 emission from power plants will be reached in the year 2010, after which it will decline as nuclear power plants become the predominant energy source. The above estimate, made in 1970, differs from a previous 1967 estimate (Reference 2) primarily in a shift in the peak year of coal consumption from 1990 to 2010. This discrepancy is due to the slower utilization of nuclear plants than originally predicted.

Power plants burning coal and oil are the largest single source of man-made SO_2 released to the atmosphere, and consequently the development of methods for reducing the quantity of this source of air pollution has a high priority in order to meet standards set by the Air Quality Act of 1967, as well as other national and regional standards which are currently being formulated. The current practice in urban east coast areas has been to use low sulfur fuels as a means of reducing the total SO_2 emission. This technique has proven successful and will continue to be used in many urban area power plants where other methods would not be either feasible or economical. However, the present and future availability of low sulfur fuels (both coal and oil) is limited, and would not be adequate to provide the degree of nation-wide abatement in SO_2 emission required to meet air quality standards now being established.

Sulfur oxide emission from power plants can be controlled in several ways among which are: the removal of sulfur from fuels before combustion; removal of SO_2 from the combustion gas; and the use of high stacks and remote power plant sites for gas dispersion. The first approach is being used with oil and gas fuels but has not been successfully developed for use on high sulfur coals. The present report is primarily concerned with the impact of the use of processes now under development on the reduction of SO_2 emission from power plant stack gas. Since even the most efficient of these processes will only reduce the SO_2 content to the level of several hundred parts per million, they must be used in conjunction with high stacks and judicious site location to ensure adequate dispersion to meet SO_2 ground level air quality standards.

References No. 2 and 3 give estimates of potential SO_2 emission levels and the amount of reduction considered feasible using various control methods. The basis of prediction used in this report is geared to SO_2 emission control by removal from the stack gas by any of the processes covered in the report. The predicted reduction represents the ultimate that may be achieved by these methods if applied where feasible on existing power plants and on all new plants which become operative after 1975. It is assumed that the technology of the SO_2 removal processes under consideration will be adequately established for commercial use by 1973, allowing two years for installation on existing plants by 1975 and on all new plants now in the planning stage which will become operative by 1975 and thereafter. Assuming limited abatement in SO_2 emission, the level of total SO_2 emission from coal and oil burning power plants will have reached 30.2 MM tons/year by 1975. A recent survey (Reference 4) indicated that about 75% of the present U. S. generating capacity from existing power plants over 200 MW capacity is amenable to some type of SO_2 removal process based on area requirements only.

When consideration is given to other factors such as cost, waste disposal capabilities, etc., an optimistic estimate would be about 35% of the total existing generating capacity could be adapted to some type of SO_2 removal installation. Assuming that 35% of the existing SO_2 emission from power plants in 1975 could be placed under control removing 90% of the SO_2 content of the combustion gas, and that 100% of all new plants built from 1975 on would be placed under similar control, it would be possible to reduce the level of SO_2 emission from power plants to about 15 MM tons/year in 1975. The emission level would gradually increase to a maximum of 25 MM tons/year in 2010, at which time the use of fossil fuels would decline and nuclear power plants would predominate. If none of the existing power plants are placed under control, but all new plants built from 1975 on are, the total SO_2 emission from power plants would be reduced to about 20 MM tons/year in 1975, increasing to a maximum of 30 MM tons/year in 2010. Further reduction in the SO_2 emitted could be effected by increasing the control process removal efficiency and by the use of lower sulfur fuels. The 15 to 25 MM tons/year SO_2 emission range is in reasonable agreement with previous estimates which assumed the application of maximum control methods. The difference is largely due to the fact that peak SO_2 emission is to be reached in 2010 rather than 1990 as originally estimated.

The total SO_2 removed from power plant flue gas would range from 15.5 MM tons/year in 1975 to 92.8 MM tons/year in 2010. The actual net recovery of SO_2 as equivalent sulfur or sulfuric acid from the various removal processes under consideration ranges from 0% for the wet and dry limestone processes to 70-90% for the various non-throwaway type processes. Therefore, if the wet limestone process were used, its impact would not be on the existing sulfur or sulfuric acid supply/demand balance but on its possible effects as a ground water pollution source. The very large quantities of $CaSO_4$ and possibly $MgSO_4$ produced as a by-product of this removal process would present disposal problems which must be considered in their relation to the surrounding environment.

Using an average value of 85% SO_2 recovery for the regenerable type processes, the equivalent sulfur recovery would be 6.6 MM tons/year (1975) and 10.8 MM tons/year (1980). This compares to an estimated total U. S. sulfur consumption of 13.4 MM tons/year (1975) and 16.2 MM tons/year (1980). Beyond 1980, the recovered sulfur from power plants alone would exceed total U. S. consumption. The impact of such large quantities of sulfur would seriously disrupt the existing market requiring a complete restructuring of the supply sources.

VII. ADVANCED POWER CYCLES

The report entitled, "Technological and Economic Feasibility of Advanced Power Cycles and Methods of Producing Nonpolluting Fuels for Utility Power Stations" has been reviewed from a different viewpoint than were the reports covering the various sulfur dioxide removal processes. The multiplicity of systems and plant cycles covered in this report coupled with the higher priority assigned to the SO_2- removal processes made it impractical in terms of time and manpower expenditures allocated to Task #5 to examine these systems in the detail applied to the sulfur dioxide removal processes. Also, since many of the conclusions reached are based on predictions of future costs and future technology, it is more appropriate to comment on the general concepts involved than on the specific systems, power cycles or economic evaluations.

Fuel Desulfurization Process

The main concept presented in this section is that the ultimate goal for a desulfurized fuel for utility power plant application lies in producing a desulfurized gaseous fuel. We agree with this "clean fuel" goal, particularly in terms of producing a high pressure, high heat content, pipeline gas for the following major reasons:

1. With conventional power plants of modern design capital costs for a gaseous fueled plant are substantially (about 30%) lower than for a solid or liquid fueled plant. This margin will probably prevail for plants utilizing advanced cycle concepts, assuming they could use solid or liquid fuel. Also, many advanced cycle plants may require gaseous fuels.

2. Considerable effort is currently being expended in the development of gasification processes for solid and liquid fuels and many potentially attractive processes are now under consideration for the production of synthetic natural gas (SNG). The commercialization of these processes and/or the development of new sources of natural gas will increase the economic attractiveness of gaseous fueled power plants.

3. The production of the equivalent of natural gas by gasification of solid or liquid fuel will make power plant siting less dependent on the location of the fuel supply since existing or new piping networks can economically distribute the fuel to optimized power plant locations.

The concept of a gasification plant producing low BTU gas for use by an adjacent, close-coupled power plant may appear to be economically attractive and may indeed be so for the "early years" when the plant is base loaded. However, experience indicates that as plants age their utilization factor decreases. Thus the close-coupled gasification-power plant design would have to include "intermittent power production" capabilities as well as face the potential obsolescence of the combined facility as opposed to only the power plant if it and the gasification plant were truly independent.

Advanced Cycle Power Systems

Thermodynamic fundamentals indicate that the greater the difference between the temperature at which heat is added to a power cycle and the temperature at which heat is rejected from the power cycle the greater is the potential thermal efficiency of the cycle. Since the temperatures at which heat can be rejected from the cycle are set by the environment, the efforts at improving power plant efficiencies have been largely directed toward increasing the temperature at which heat is added to the cycle. Along with increasing the temperature and pressure at which the steam is generated and increasing the superheat temperature, attempts were made to develop "topping" cycles using fluids, such as mercury, with pressure-temperature characteristics more suitable than water to high temperature operation. The problems associated with mercury systems were such that the mercury topping cycle was abandoned, and pre-1950 efforts were directed toward improving the steam cycle itself. With the advent of larger, more reliable, gas turbine renewed interest developed in the topping cycle using the "hot gas" system to "top" the steam system.

We agree with the conclusion that future power plants will probably employ advanced cycles using both gas turbines and steam turbines for the following reasons:

1. Many studies have been made, here and abroad, to evaluate such cycles and combined gas turbine-steam turbine plants are now commercially available in modest size (such as the 180 MW STAG power plant from General Electric Co.). There is no question that these plants have a higher potential efficiency than the straight steam power plant without regard to whether the practical maximum steam temperature is 1000°F, 1100°F or 1200°F.

2. Since fuel costs are a major factor in the cost of generating power, utilities can be expected to favor cycles yielding higher efficiencies, with a pollution-free effluent representing an additional advantage.

3. Cycles of increased complexity, such as tertiary cycles, may possibly be designed to have higher efficiencies than the simpler gas turbine-steam turbine cycle, but it is extremely unlikely that the efficiency advantage would justify the added complexity. The past history of the mercury cycles is not easily forgotten. Most utilities will be reluctant to accept systems utilizing potentially hazardous fluids such as ammonia. Their lack of experience in handling these fluids plus the added equipment requirements of tertiary cycles make them more of academic than practical interest.

Despite the long-term potential of combined gas turbine-steam turbine power plants and the increased use of gas turbine power for handling peak loads, the lack of experience with large size, base loaded, gas turbines should not be ignored. Considerable reluctance may be expected on the part of utilities to being among the first to commit themselves to carrying a base load with gas turbine driven generators.

Integrated Power Stations

It is not clear, particularly at this stage of development of gasification processes, that close integration of the gasification plant with the power plant would result in an optimized system based on the anticipated useful life of the plant. Better overall on-stream reliability may be attained by producing pipeline gas for delivery to gas distribution systems and drawing the power plant fuel from these gas distribution systems. Utilities marketing both gas and electric power may find this kind of system particularly attractive.

Research and development programs related to high pressure gasification and desulfurization of solid and liquid fuels should be strongly supported as these will directly affect air quality without regard to the type of power plant in which the gasified fuel is burned.

Research and development programs related to development of advanced materials and cooling techniques should also be supported since such materials and techniques could probably be utilized in the design of the gasification plant equipment, as well as in the design of advanced gas turbines.

Considering the current level of experience with Lurgi coal gasifiers and the fairly extensive experience with gas turbine systems, it is questionable if there is very much to be gained by constructing a pilot or demonstration plant at this time. Detailed design studies, however, to develop relatively firm economics for a full-scale integrated gasification-power plant would be most useful in pointing up specific problem areas and major cost items requiring more intensive development and additional design studies.

VIII. REFERENCES

(1) "Abatement of Sulfur Oxide Emissions From Stationary Combustion Sources" National Academy of Engineering, National Research Council, Washington, D.C., 1970

(2) Rohrman, F.A., Steigerwald, B.J., and Ludwig, J.H. "SO_2 Pollution: The Next 30 Years", Power, May 1967, p. 82

(3) Hangebrauck, R.P. and Spaite, P.W., "Controlling the Oxides of Sulfur", JAPCA, Jan. 1968, Vol. 18, No. 1, p. 5

(4) M.W. Kellogg Co., Letter No. K-5-6, Applicability Survey Report, March 3, 1971

IX. APPENDIX

LIMESTONE - WET SCRUBBING PROCESS

A. PROCESS SECTION

1. Process Description (see MWK Dwg. No. PD-108-D)

The limestone-based wet scrubbing process involves the removal of sulfur dioxide and fly ash from a coal-fired boiler stack gas through the use of an aqueous slurry of raw limestone or lime. The overall reactions involved in the SO_2 removal step are as follows:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + SO_2 + 1/2\ O_2 \rightarrow CaSO_4$$

The particular flow scheme chosen for evaluation in the study for APCO involves the injection of raw stone into the boiler to achieve complete calcination and partial sulfation. The remainder of the SO_2 removal is accomplished via liquid phase reactions which occur in the scrubber system (see Chemistry Section of this write-up for a discussion of the various reactions possible).

Raw limestone is unloaded into hoppers and transported to storage silos and feed silos by belt conveyor. Limestone is fed to pulverizers to reduce its size to 70% minus 200 mesh, where it is mixed with preheated air for drying and transporting to boiler injection ports. It is assumed that two conventional 500-MW pulverized-coal fired boilers will be used in this new installation, hence the process flowsheet is drawn to show two parallel stack gas treating trains.

The boiler stack gas downstream of the air preheater contains fly ash and other solid components ($CaCO_3$, CaO, $CaSO_4$). The main flow stream from each 500-MW boiler is split into three parallel scrubbing trains, the number being set by the maximum feasible scrubber size. The stack gas is first cooled from 310°F to 177°F in an indirect gas-liquid exchanger employing circulating water as the heat transfer medium. The gas will then be fed to a countercurrent scrubber for removal of inert solids and completion of the $CaO-SO_2$ reaction. The particular scrubber design selected must have a high solids removal efficiency (>99%) to eliminate the expensive precipitator installation in a new plant. Effluent gas from the scrubbers is heated to 250°F to achieve satisfactory plume dispersion by the circulating hot water system, after which it is sent to the stack via induced draft fans.

The liquid effluent from each scrubber tower is sent to hold tanks wherein several minutes residence time is provided to achieve controlled crystallization of $CaSO_4$ reaction product on existing particles. This design will hopefully minimize deposition and plugging in liquid circulation lines. A combined purge stream from the scrubber circuit is pumped to a settling pond for removal of solids, e.g., fly ash, $CaSO_4$ and $Ca(OH)_2$ formed from hydration of the unconverted lime.

The settling pond overflow is recycled to the scrubber system on the premise that local water pollution considerations would not tolerate the discharge of $CaSO_4$ and $MgSO_4$ from the limestone streams into an adjacent watercourse. Make-up process water is added to the system to compensate for the evaporation loss from the settling pond plus the scrubber water vaporization resulting from direct gas cooling.

2. Process Design Bases

The base case flowsheet developed for wet limestone scrubbing is for a new 1,000 megawatt installation with pulverized limestone injection into the boiler. There are other process variations worthy of investigation, e.g., limestone or pre-calcined lime injection into the slurry circuit, however the Kellogg base case was selected to be identical with the base case in the TVA con- ceptual design study (1)* The TVA process design bases were maintained wherever possible, with exceptions noted below, and were scaled-up from 200 MW to 1,000 MW generation capacity.

*** Refers to references at end of section**

Another reason for selecting the boiler injection process scheme as the base case is that it is the most advanced concept having been demonstrated in two commercial plants (125-140 MW) by Combustion Engineering. Unfortunately, no information from these plants was made available to Kellogg during the present study for APCO, and the commercial experience could not be factored into this evaluation. The ability to include this experience would shed considerable insight into the potential problem areas discussed in a subsequent section of the write-up.

The following is a list of specific process and equipment design bases used with amplification provided in the section entitled design rationale:

a) Limestone addition rate $\simeq$ 110% stoichiometric

b) Limestone composition: 91.8% $CaCO_3$ (dry basis)
10. % moisture

c) 100% Sulfur in Coal evolves in Stack Gas (SO_2+SO_3)

d) 71.6% Ash in Coal evolves as Fly Ash

e) 100% Conversion of $CaCO_3$ to CaO in Boiler
25% Conversion of CaO to $CaSO_4$ in Boiler

f) Stack Gas Ductwork: Use 3 main ducts from 500 MW Boiler (3 parallel trains). Provide separate cooler, scrubber, reheater and induced-draft fan per train (6 parallel systems total - 1,000 MW)

g) Stack Gas Cooler and Reheater Design; Indirect exchange against circulating water (can also add glycol), single pass gas side cross-flow unit, overall transfer coefficient 8 Btu/hr x °F x ft^2, 220,000 ft^2 surface/unit (6 Coolers and 6 Reheaters required - 12 identical units), Finned tube bundle: 40 ft long x 12 ft wide x 8 ft deep,
Cooler Design ΔP 4 inches H_2O (includes gas distributor)
Reheater Design ΔP 4 inches H_2O (includes gas distributor)

h) Scrubber Design (6 identical units req'd)
UOP TCA Contactors
Vessel size: 15 ft deep x 34 ft x 40 ft high with center partition (2 Gas Inlets & 2 Gas Outlets)

3 contacting stages of 1-1/2 inch plastic spheres
Design Inlet Liquid/Gas ratio = 6.12 lbs/lb.
Design SO_2 Removal = 90 %
Design Particulates Removal = 99+%
Design ΔP (overall) = 9" H_2O (including Demister Pad)
Design Inlet Liquid conc. = 10.0% Solids

i) Recirculation System

Provide separate tank per Scrubber for optimum control
Size liquid lines for 8 ft/sec maximum velocity
Design tank residence time = 4 minutes

j) Rotating Equipment

Use 70% efficiency for centrifugal plumps and fans (assume motor drives for estimating purposes)

Induced-draft fan head requirements (incremental only);

Gas Cooler	4 in H_2O
Scrubber	9 in H_2O
Gas Reheater	4 in H_2O
New Ducts	6 in H_2O
Incremental ΔP	23 in H_2O static pressure

k) Limestone Feed System (TVA Design Bases)

Unloading Hoppers (2); 250 tons total capacity
Storage Silos (2); 3,000 tons total capacity (60 hr supply)
Feed Silos (2); 400 tons total capacity (8 hr supply)
Pulverizers (2); design for 70% minus 200 mesh
Injection Air = 0.52 lbs/lb solids
Classifying Air = 0.10 lbs/lb solids

l) Solids Disposal System

10. wt % solids concentration in sluice water lines to settling pond

Pond evaporation loss = 620,000 lbs/hr (5 x pond evaporation loss calculated in TVA 200 MW study)

Additional pond area (205 acre-ft/yr) to be purchased and developed to accommodate additional solids.

3. Design Rationale

In this section, a more detailed discussion is presented to explain the judgement factors behind the specific process and equipment design bases cited in the preceding section. The discussion is broken down into the various process systems of the base case flowsheet.

a) Limestone Feed System

The design bases for the raw limestone surge hoppers and storage silos were taken directly from the TVA conceptual design report. Similarly, the design basis for the limestone grinding and injection system is as specified in the TVA report. There is no need to achieve a finer degree of grinding than specified as the SO_2 conversion in the boiler is not critical in the wet limestone process. A number of suggested improvements in the limestone handling equipment for a 1,000-MW plant is presented in the Mechanical Review section of this report.

b) Boiler System

Essentially 100% calcination of raw limestone was assumed followed by 25% conversion of CaO to $CaSO_4$ in the boiler. These assumptions are based on the most reliable pilot plant and full-scale data from the dry limestone process test program. The exact conversion in the boiler is not critical as the desired overall SO_2 removal of 90% has been demonstrated in both ICI-Howden pilot plant tests (1) and Combustion Engineering commercial plant tests.(1) It was further assumed that the only deleterious effect of limestone injection is the increased solids handling, and that boiler operability(effect on firing, deposition) would not be adversely affected.

c) Stack Gas Cooler-Reheater System

The indirect circulating water system recommended in the TVA report based on studies of six different heat transfer schemes was accepted without further evaluation. The temperature limits were established in accordance with TVA's recommendation of 250°F stack gas temperature to achieve buoyancy for plume dispersion. The overall design heat transfer coefficient of 8.0 seems reasonable based on air cooler design experience. Single-pass gas crossflow unit having finned-tube bundles with 40 ft tube length were used (rather than 20 ft) to minimize the number of rows and the gas phase pressure drop. Even so, the resulting design yields 4 inches water ΔP per unit as compared with 2 inches water ΔP in the TVA design. The higher pressure drop was used in establishing the fan static pressure requirements.

d) Scrubber Design and Recirculation System

The TVA report recommends the UOP TCA Contactor (flooded-bed design) as the optimum unit in a limestone slurry service based on good pilot plant performance results in an actual stack gas service.(2) However, the specific design conditions specified by TVA were found to be inadequate when compared to the cited pilot plant results. It was necessary to increase the liquid circulation rate by 50% (L/G from 4.08 → 6.12 lbs/lb) and the number of contacting stages from 2 to 3 to achieve 90% minimum SO_2 removal and 99+% solids removal. The latter removal efficiency is essential as no mechanical separators or precipitators are proposed for the new plant design. The proposed new design results in higher pressure drop (9 inches H_2O vs. 6 inches H_2O) including the loss through a demister pad.

The scrubber inlet liquid concentration of 10.0 wt % solids taken from the TVA report was based on ICI-Howden pilot plant data. The concept of a hold tank designed for 3-5 minutes residence time to achieve controlled crystal growth demonstrated at ICI-Howden was also incorporated by TVA. The slurry solids content should affect both reaction kinetics and crystallization rates, however since there are insufficient data to optimize this variable, the TVA design bases were accepted.

e) Solids Disposal System

The ability to sluice a 10% solids slurry of "reactive ash" (containing CaO, $CaSO_4$) to the disposal pond without major plugging problems is a critical technical consideration. Based on successful ICI-Howden experience, the 10% solids concentration was accepted as a design value. The disposal pond water evaporation loss was also taken from calculations in the TVA report and pro-rated to 1,000 MW capacity.

Since the pond evaporation loss is 70% of the process make-up water, this figure could be decreased by the following means; providing deeper ponds (less area), prethickening the solids purge stream, and use of an additive (long-chain alcohols) to decrease the vaporization rate. However, the TVA proposal of sending the pond overflow water to an adjacent watercourse was deemed unacceptable because of build-up of sulfates, and a pond recycle stream is shown in the present design. Additional acreage for increased solids disposal would have to be available otherwise expensive transportation schemes would be required. The additional disposal pond area specified was pro-rated directly from the TVA report.

4. Process Appraisal

The limestone-wet scrubbing process is one of the most advanced SO_2 control processes in that it has been demonstrated in several pilot plants and commercial installations. It has the obvious attractiveness of being a "throwaway process", and the additional advantage of controlling particulates emission without installation of an expensive precipitator. Based on the TVA conceptual design study, the investment for limestone-wet scrubbing process equipment should be significantly lower than the regenerable SO_2 control processes. There is ample incentive for continued funding of development programs, process optimization studies and demonstration plant testing of this process.

The major disadvantage of limestone-wet scrubbing is the problem of water pollution and solids disposal associated with a throwaway process. There are other serious problems involving equipment operability which have been indicated from the limited information published from the Combustion Engineering demonstration plants. The problems have involved equipment fouling and scaling, with the problem areas described in greater detail below. Suggested research and development areas to improve the limestone-wet scrubbing process technology are also incorporated into the following discussion.

a) Potential Problem Areas

(1) Boiler Injection

The flowsheet chosen for evaluation shows boiler injection of the limestone additive as this concept has been demonstrated on a commercial scale. This process scheme raises obvious concern about the effect of the additive on boiler operability, e.g., effect on firing pattern, slagging, deposition, heat efficiency. Deposition problems were experienced initially during the TVA tests of the dry limestone process in the Shawnee unit and at other test installations. Attempts at generalized predictions of limestone-coal ash deposition tendencies have been unsuccessful, so this must be considered a potential problem area in a new installation. The operating problems may be controllable by use of additional soot blowing capacity.

One means of avoiding the boiler injection problems is by limestone addition directly into the scrubber circuit. This scheme represented the alternate case evaluated in the TVA design study. The investment for the alternate case was higher mainly because of the greater limestone handling requirements. That is, higher stone injection rates were specified for the alternate case (130% stoichiometric vs. 110% base case) because of the lower reaction rates observed in pilot studies, possibly due to a slower rate of solution with limestone than lime. There are ways of improving this kinetic limitation, e.g., finer grinding of raw stone, increased scrubber residence time. It is felt that the concept of limestone injection into the scrubber system could well represent the optimum process configuration and merits additional testing.

(2) Scrubber Design Optimization

The other major incentive for use of a wet scrubbing process is the cost reduction possible by eliminating an electrostatic precipitator. This presumes that better than 99% (by weight) of the particles can be removed in a wet scrubber. Such claims have been made by various scrubber vendors and have been achieved in pilot plant tests of a mobile-bed scrubber (Hydrofilter or TCA Contactor).

There are several areas of concern relating to the scrubber design. Firstly, 99 weight percent removal of particles with a typical fly ash size distribution would still leave 10-30% of the smallest particles ($<2\mu$ size) in the gas which could create problems with the visible plume appearance. Secondly, although mobile-bed scrubbers have performed well on a small scale, there could be flow distribution problems in scale-up to commercial power plant units. Such problems have already been encountered with the Hydrofilter (flooded glass marble bed) in Combustion Engineering's commercial operation, and could also occur with the UOP TCA Contactor specified in the TVA design. Consideration should be given to testing alternate scrubber designs which have a better established scale-up basis, e.g., venturi devices possibly including staging, or tray-type contactors with or without impingement baffles.

The other potential scrubber operating problem is solids deposition in the circuit. Major plugging problems have been encountered in the Combustion Engineering process in the region of the scrubber gas inlet. It has been postulated that the increase in pH occurring at the point of lime addition will tend to precipitate calcium sulfite and sulfate. This would indicate another advantage for injection into the slurry circuit, preferably between the scrubber and the hold tank, which would ideally cause precipitation to take place on existing crystals in the hold tank. This operating technique permitted the ICI-Howden process to run with a minimum of plugging problems, but the factors controlling crystallization rates need further study.

(3) Stack Gas Reheat Design Optimization

Various direct and indirect heat exchange schemes were studied by TVA to select the optimum system for stack gas reheat. The system selected was a cyclic liquid (hot water possibly containing glycol) indirect heat exchange system to recover the stack gas heat. The heat exchanger costs were derived by TVA assuming carbon steel tubes for the gas cooler and reheater. This assumption may be too optimistic considering the presence of free CO_2 and SO_2 in the gas which would result in the formation of weak acids as the dew point is approached in these units. Upgrading the tube material to a stainless alloy could increase the exchanger investment several-fold, and make it more attractive to consider direct fuel combustion (oil or gas) ahead of the stack as the source of heat. The TVA further assumed that 250°F was the reheat temperature necessary to achieve the desired ground-level SO_2 concentration, which is also determined by other variables. For example, use of a taller stack and lower reheat temperature could favor selection of a direct combustion reheat system.

The large finned-tube exchangers specified in the proposed process design also present several operating problems, i.e., gas distribution across the bundle, fouling by the fly ash and reaction products. Some pilot plant experience has suggested that deposits could be removed by intermittent water washing using boiler condensate. The other alternative would be to specify expensive soot blowing equipment. It seems obvious that a process optimization study of means to provide gas reheat would be justified.

b) Research and Development Areas

The preceding discussion cites a number of potential problem areas in the limestone-wet scrubbing process which warrant further study. Specific research and development programs to satisfy these needs are summarized below. These suggested areas of study are weighted to provide data on the scrubber system injection process, which is judged to have the greatest chance of technical success at this time.

(1) Kinetic data on the sulfation reaction step with addition of either $CaCO_3$ or CaO to solutions of various total solids content.

(2) Kinetic studies on crystallization of $CaSO_3$ and $CaSO_4$ from supersaturated solutions in the presence of other solids.

(3) Tower design data on particulates and SO_2 removal efficiency for various types of contactors.

(4) Studies of plume dispersion as a function of stack gas temperature, velocity, stack height and atmospheric conditions.

5. Mechanical Review

a) Raw Limestone Storage and Handling

The storage capacity provided for raw limestone is 60 hours at plant capacity. This is relatively small and it is suggested that a minimum of one week's storage be provided. This would insure against equipment breakdown at the source of supply, transportation delays, strikes, etc. It can be a supplemental pile used in conjunction with active storage in a silo, or it can be a working pile.

One week's storage would require approximately 2000 tons for a 200 MW plant and 10,000 tons for a 1000 MW plant. These large tonnages are most economically stored in open piles, stacked by a belt conveyor. If space for piles is unavailable, silos can be used, but they are expensive.

The added storage will increase the cost of the limestone system considerably, and this should be provided for in any cost estimates for the process. The major increase will be for the more extensive conveying and elevating systems, reclaim tunnels and feeders.

When the limestone contains fines, freezing will occur during winter months in northern climates. This may require car-thawing facilities and may also dictate that the stone be stored under cover or in silos. If this is not possible, then special precautions are needed to prevent the plug-up of reclaiming feeders with large, frozen masses of limestone.

Another factor to be considered in space and cost requirements for the larger plants is the method of delivery. A 1000 MW plant will use approximately 10,000 tons per week, or 2000 tons per day, on a 5-day basis. This will probably require rail delivery with extensive trackage and a rail-car unloading hopper. If coal is received by rail, the coal unloading facilities should be designed to handle the limestone also.

On plants larger than 1000 MW, the limestone might be delivered on a unit-train basis. A 2000 MW plant would use 2 unit train loads per week. The R.R. trackage, high-rate unloading facilities and storage of stone then becomes a major materials handling problem. The unit train concept may make it possible to economically install this process even though the limestone supply is distant from the power plant. It also raises the interesting possibility of reloading the train with waste for disposal at a distant point.

b) Dust Collection

Dust suppression and dust collecting equipment are not mentioned, except for the items integral to the grinding circuit. The limestone unloading station may require a dust suppression system and all conveyor loading and transfer points should have dust hoods vented through a bag filter.

c) Ground Limestone Injection

The ground limestone feed bin may not discharge in a reliable manner due to arching and rat-holing of the material above the discharge opening. It should be provided with an activated bin bottom to assure a steady feed to the injection system.

The method used for dividing six streams to the injection nozzles is questionable. A single volumetric feeder meters the total amount into an air stream to a flow-splitting tank. This tank theoretically divides the stream into six equal flows. Details of the tank are lacking, but it appears to be a single vessel with one inlet and six discharges.

Much closer control over the solids flow rate to each nozzle would be obtained by providng an individual feeder for each, with individual conveying lines. This would give the boiler operator the added advantage of individual control if he desired to vary the rate to any boiler zone.

The above comments apply only to boilers fired by pulverized fuels, with multiple injection points. Cyclone-fired boilers were not studied in this report.

d) Wet-Grinding Facilities

The limestone wet grinding facilities would be improved if the feed bin was elevated to feed the mill directly. The weigh feeder will then discharge to the mill, eliminating the bucket elevator and its corresponding time lag. Also, the elevator is a high-maintenance item and its removal eliminates the mill's dependency upon the elevator's operation.

If possible, the elevator feeding the bin should be replaced by a belt conveyor. A conveyor offers better reliability with less maintenance.

An alternate method should be investigated for closing the wet-grinding circuit for the mill. The spiral classifier used in the process is inflexible in its relation to the mill due to the required slopes in the feed launder and the discharge chute. If space limitations in a retrofit installation preclude the use of this type of unit, wet-cyclones should be investigated. They require much less space and have greater flexibility of location.

e) Waste Storage

The waste storage requirements are very large - approximately 785,000 tons per year for a 1000 MW plant. Since these solids are handled as a slurry and contain materials other than fly ash, there is a risk of ground water contamination. For example, if dolomite is used the magnesium sulfate produced in the reaction with SO_2 is soluble. Also, unreacted limestone will enter the pond as calcium hydroxide, creating a pH problem. Existing plants which had no trouble with fly ash disposal may require new ponds lined with membrane or an impervious blanket.

More information is needed on the settling characteristics of the solids. Cyclones located at the disposal site might reduce the settling area required. They are portable and easily relocated as the solids build up. They are particularly useful where space for thickeners is not available. Many minerals beneficiation plants utilize them to build dikes for containment of tailings.

B. CHEMISTRY

1. Qualitative Process Description

The SO_2 from stack gas is transferred to the aqueous phase where it is "fixed" by a very rapid reaction with basic ions like OH^- and HCO_3^- to form HSO_3^- and $SO_3^=$ ions. Additional SO_2 may dissolve to form H_2SO_3. In a practical scrubber situation it is not possible to supply enough of these basic ions in solution to react with all of the SO_2 in the gas. This is because the amount of liquid is limited by flooding considerations and the concentration of basic species is controlled by the limited solubilities of the alkaline earth hydroxides and carbonates (3). To circumvent these limitations a slurry containing basic solids which will react and replenish the ions consumed by SO_2 is usually fed to the scrubber. The rate of dissolution of these solids is the limiting chemical step in determining the efficiency of the scrubbing process (4).

Most process concepts involve injection of limestone or dolomite into the hot flue gas at a temperature high enough to decompose the carbonates to form oxides. Any SO_2 that is reacted with the solid oxides before it reaches the scrubber is effectively removed and need not be considered in the scrubbing process. This may account for nearly 20% of the SO_2 removal (5). The remaining oxides and all of the fly ash are trapped by the scrubber liquid.

Inasmuch as the mechanism for dissolution of calcium and magnesium oxides involves an initial slow hydration step, residence time in the process is usually provided by installation of a scrubber effluent holding tank. Part of the slurry from the holding tank, which contains the alkaline earth hydroxides in suspension, is then used for the scrubber liquid feed. It is normally assumed that these hydroxides will dissolve rapidly enough to be used in the scrubber, but this is open to question (1,2).

Alternate process concepts which involve addition of uncalcined limestone, or dolomite to the scrubber depend upon the dissolution of these compounds by a liquid saturated with CO_2. Very little data have been gathered to demonstrate this concept.

The HSO_3^- and $SO_3^=$ ions formed from the SO_2 are further reacted along a number of pathways resulting in a final transfer of most of the sulfur to the solid phase which is withdrawn from the system. Some of these pathways are:

1. $SO_3^= + Ca^{++} \longrightarrow CaSO_3(s)$
2. $HSO_3^- + Ca^{++} \longrightarrow CaSO_3(s) + H^+$
3. $SO_3^= + Mg^{++} \longrightarrow MgSO_3(s)$
4. $HSO_3^- + Mg^{++} \longrightarrow MgSO_3(s) + H^+$
5. a. $SO_3^= + 1/2\ O_2 \longrightarrow SO_4^=$
   b. $Ca^{++} + SO_4^= \longrightarrow CaSO_4(s)$
6. a. $HSO_3^- + 1/2\ O_2 \longrightarrow SO_4^= + H^+$
   b. $Ca^{++} + SO_4^= \longrightarrow CaSO_4(s)$

A small amount of the sulfur remains in solution - principally as $SO_4^=$ ion - and is removed as a purge stream. This is particularly true with dolomitic limestones where most of the sulfate made by reactions 5a. and 6a. is removed as a solution of $MgSO_4$ (3).

Fly ash, which is caught by the scrubber, may partially dissolve and influence which of the pathways given above is predominent in the overall process. The influence may be catalytic - such as the acceleration of sulfite oxidation in the presence of Mn^{++} ions - or in shifting solubilities by mass action or ionic strength effects. In addition, chemical reactions involving fly ash components may lead to undesired solids - like hydrous oxides and hydroxides - which cause trouble in subsequent filtration operations. Since alternate process concepts may consider removal of fly ash prior to scrubbing it should be pointed out that there are possible advantages to their presence. Among these is the reduction of scale formation by providing additional surface for crystallization and a mild abrasive action on process equipment.

Other components of the flue gas are partially absorbed by the scrubber and influence the chemistry of the scrubbing process. The large excess of carbon dioxide in the gas reacts rapidly with OH^- and $CO_3^=$ ions in the scrubber feed to form HCO_3^- ions which are the principle basic species present in the scrubber for reaction with SO_2. Until all of the HCO_3^- ions have been consumed by the SO_2 a buffer system between HCO_3^- ions and CO_2 keeps the pH between 6 and 7. Oxygen in the gas converts dissolved sulfite species to sulfate which changes the pathway by which the sulfur is removed from the system. If this oxidation could be prevented the scrubber might have a greater capacity - since the H^+ ions liberated by reaction 6a, consume HCO_3^- ions - but the sensitivity of oxidation to accidental catalysts present in the fly ash makes this difficult. Nitrogen oxides are partially removed by the scrubber. The amount removed is probably related to the amount of NO oxidation that has taken place before the flue gas enters the scrubber. When NO_2 dissolves it forms nitrate ions and a mixture of nitrite ions and nitrous acid. The chemistry of subsequent reactions between the latter 2 species, dissolved SO_2 and HSO_3^- ion in the presence of oxygen is not well known, but, since nitrite and sulfite are known not to be stable in the presence of each other in acid solutions it is usually assumed that only NO_3^- remains (3). It is interesting that experiments at Battelle (4) appear to show that NO_x enhances the capacity of a calcium hydrate solution for SO_2 absorption by 70% beyond theoretical.

2. Equilibrium Limitations

It has been calculated that an equilibrium partial pressure of SO_2 above a liquor of pH 4 to 4.5 is less than 300 ppm - equivalent to 90% removal (3). In the scrubbing system described this situation would occur after reaction with SO_2 had depleted all of the basic species in solution and additional SO_2 had dissolved to form H_2SO_3. The maximum concentration of basic species that can be obtained in solution in the scrubber feed is controlled by solubility relationships between calcium and magnesium hydroxides and carbonates in the presence of many other solids and dissolved species. Radian Corporation (3) has developed a computer program to handle the complex equilibrium calculations involved. In general it appears that, if the scrubber feed is equilibrated in the absence of CO_2 (out of contact with flue gas), the more soluble $Ca(OH)_2$ will dissolve to produce OH^- ions as the principal basic species. At the high pH of this solution $Mg(OH)_2$ is insoluble. If insufficient CaO is available as in a high magnesium dolomite, for example, the pH is much lower; a relatively high concentration of $MgSO_4$ is found in the liquid; and the concentration of dissolved basic species is lower.

It has been assumed that precipitation of calcium carbonate does not take place when the OH^- ions in the scrubber feed are converted to HCO_3^- ions by reaction with CO_2 in the scrubber feed even though the solubility product of $CaCO_3$ may be exceeded. This assumption seems reasonable in the practical model of a backmixed reactor.

3. Rate Limitations

As stated previously, the rate limiting step in the scrubbing reaction is the dissolution of basic solids in the scrubber to replace the species lost by reaction with SO_2. If too little reaction occurs in a single pass through the scrubber,provision must be made to recycle these solids. A Battelle study concerning measurement of various rates involved in the wet-scrubbing process (4) indicates that lime in particulate form reacts readily with various sulfur species or carbonate in solution to yield a coating which inhibits utilization of the bulk of the lime. The same study recommends that further consideration be given to the importance of particle size in the overall process and to the possibility of predissolving all of the lime, or limestone in feed water. Unfortunately, due to solubility limitations, the latter recommendation would appear to involve an excessively high ratio of liquid to gas rates.

By far the slowest reaction in the standard process is the hydration of the lime taken from the flue gas by the "rain" of scrubber effluent. A large holding tank is usually provided to give sufficient residence time for this reaction. Again the Battelle study indicates that deposition of sulfate on the lime hinders the hydration process. In this case the surface coating may have been formed by exposure to SO_2 prior to contact with the hydrating liquor or by reaction between the lime and sulfate or sulfite in the liquor.

In summary it appears that a substantial amount of slurry recycle will be required in the standard process concept because of problems in reacting the lime at a reasonable rate. Alternate process concepts such as predissolving the lime or using uncalcined limestone have difficulties due to equilibrium solubility limitations. It is not clear whether the inclusion of fly ash is harmful or beneficial to overall scrubber operation.

REFERENCES

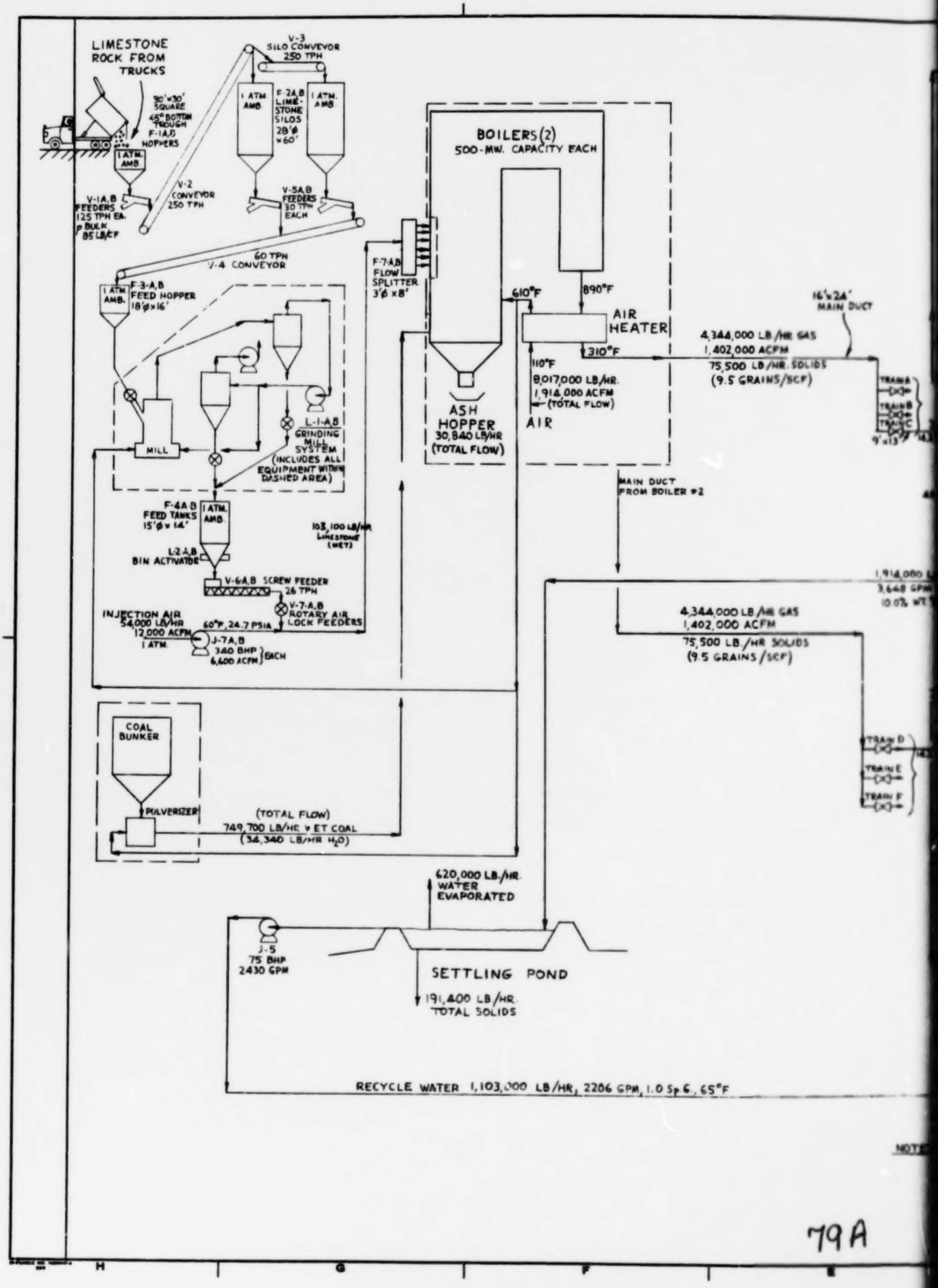
(1) "Sulfur Oxide Removal from Power Plant Stack Gas - Use of Limestone in Wet-Scrubbing Process", TVA Conceptual Design Study (1969), Final Report on Contract No. TV-29233A.

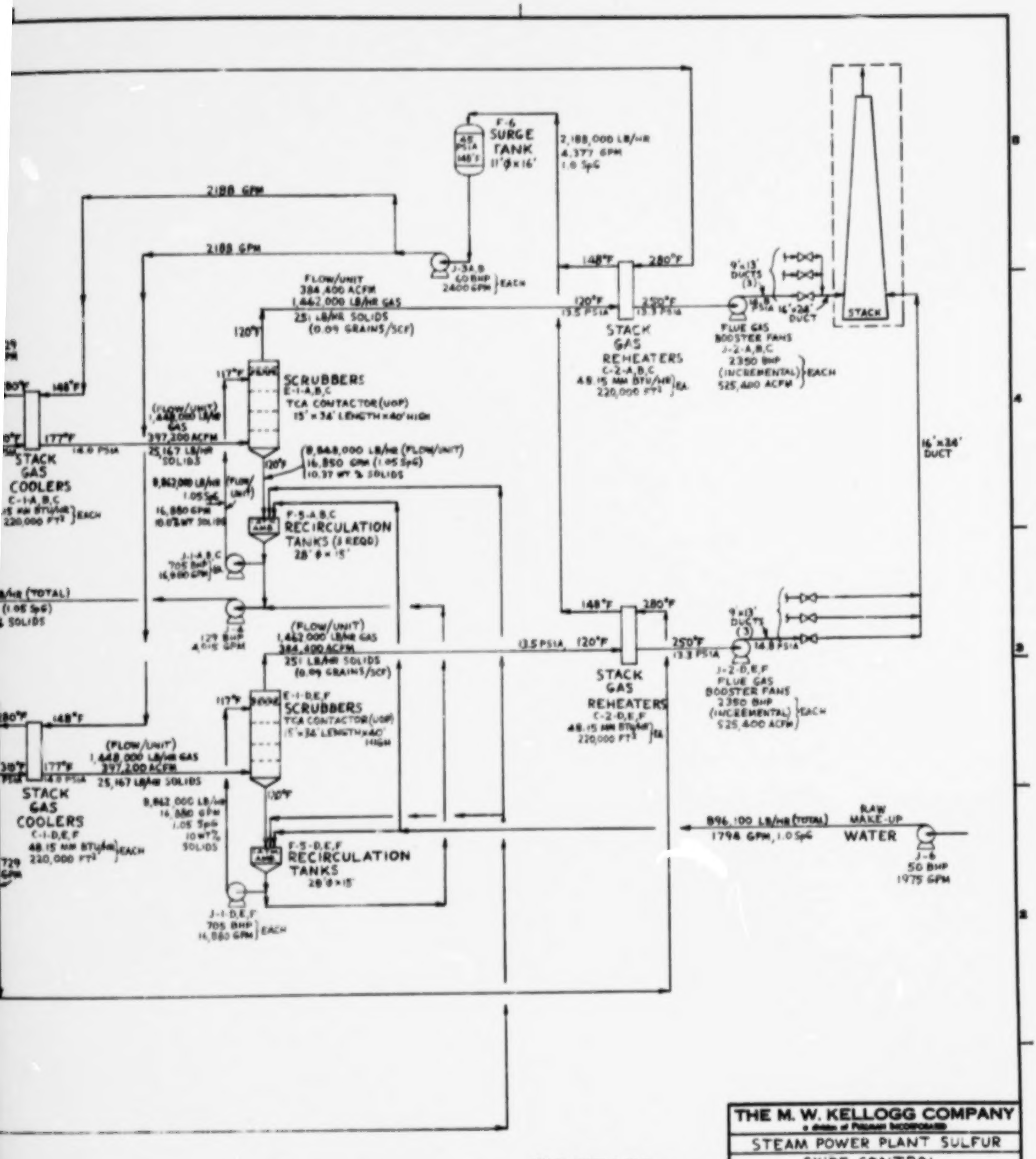
(2) Pollock, W. A., Tomany, J. P., and Frieling, G., Mech. Eng. 89 (8), 21 (1967).

(3) "A Theoretical Description of the Limestone Injection-Wet Scrubbing Process", Radian Corp., Austin, Texas (June 1970) Final Report on Contract No. CPA 22-69-138, Vol. I.

(4) "Investigation of the Limestone-SO_2 Wet Scrubbing Process", Battelle Memorial Institute, Columbus, Ohio, November 1969, Final Report on Contract No. PH 86-68-84 Task Order No. 17.

(5) "Sulfur Oxide Removal from Power Plant Stack Gas-Sorption by Limestone or Lime-Dry Process", TVA Conceptual Design Study (1968).


LIMESTONE ROCK FROM TRUCKS
30'×30' SQUARE 45° BOTTOM TROUGH
F-1A,B HOPPERS
1 ATM. AMB.
V-1A,B FEEDERS 125 TPH EA.
ρ BULK 85 LB/CF
V-2 CONVEYOR 250 TPH
V-3 SILO CONVEYOR 250 TPH
1 ATM. AMB.
F-2A,B LIME-STONE SILOS 28'ϕ ×60'
1 ATM. AMB.
V-5A,B FEEDERS 30 TPH EACH
60 TPH
V-4 CONVEYOR
1 ATM. AMB.
F-3-A,B FEED HOPPER 18'ϕ×16'
MILL
L-1-A,B GRINDING MILL SYSTEM (INCLUDES ALL EQUIPMENT WITHIN DASHED AREA)
F-4A,B FEED TANKS 15'ϕ × 14'
1 ATM. AMB.
L-2 A,B BIN ACTIVATOR
V-6A,B SCREW FEEDER 26 TPH
V-7-A,B ROTARY AIR LOCK FEEDERS
INJECTION AIR 54,000 LB/HR 12,000 ACFM 1 ATM.
60°F, 24.7 PSIA
J-7A,B 340 BHP 6,600 ACFM EACH
103,100 LB/HR LIMESTONE (WET)
F-7-A,B FLOW SPLITTER 3'ϕ ×8'
BOILERS (2) 500-MW. CAPACITY EACH
610°F
890°F
AIR HEATER
310°F
110°F
8,017,000 LB/HR. 1,914,000 ACFM (TOTAL FLOW)
AIR
ASH HOPPER 30,840 LB/HR (TOTAL FLOW)
16'×24' MAIN DUCT
4,344,000 LB/HR GAS
1,402,000 ACFM
75,500 LB/HR. SOLIDS
(9.5 GRAINS/SCF)
TRAIN A
TRAIN B
TRAIN C
9'×13'
MAIN DUCT FROM BOILER #2
1,914,000 L
3,648 GPM
10.0% WT
4,344,000 LB/HR GAS
1,402,000 ACFM
75,500 LB./HR SOLIDS
(9.5 GRAINS/SCF)
TRAIN D
TRAIN E
TRAIN F
COAL BUNKER
PULVERIZER
(TOTAL FLOW)
749,700 LB/HR WET COAL
(34,340 LB/HR H₂O)
620,000 LB./HR. WATER EVAPORATED
J-5 75 BHP 2430 GPM
SETTLING POND
191,400 LB/HR. TOTAL SOLIDS
RECYCLE WATER 1,103,000 LB/HR, 2206 GPM, 1.0 Sp G, 65°F
NOTE
H
G
F
E


F-6
SURGE TANK
11'Ø×16'
45 PSIA
148°F
2,188,000 LB/HR
4,377 GPM
1.0 SpG
2188 GPM
2188 GPM
J-3A,B
60 BHP
2400 GPM } EACH
FLOW/UNIT
384,400 ACFM
1,462,000 LB/HR GAS
251 LB/HR SOLIDS
(0.09 GRAINS/SCF)
120°F
148°F
280°F
120°F
13.5 PSIA
250°F
13.3 PSIA
STACK
GAS
REHEATERS
C-2-A,B,C
48.15 MM BTU/HR
220,000 FT² } EA.
9'×13' DUCTS (3)
14.8 PSIA
16'×24' DUCT
STACK
FLUE GAS
BOOSTER FANS
J-2-A,B,C
2350 BHP
(INCREMENTAL)
525,400 ACFM } EACH
16'×24' DUCT
180°F
148°F
177°F
14.0 PSIA
STACK
GAS
COOLERS
C-1-A,B,C
48.15 MM BTU/HR
220,000 FT² } EACH
117°F
SCRUBBERS
E-1-A,B,C
TCA CONTACTOR (UOP)
15'×34' LENGTH×40' HIGH
(FLOW/UNIT)
1,448,000 LB/HR GAS
397,200 ACFM
25,167 LB/HR SOLIDS
120°F
8,848,000 LB/HR (FLOW/UNIT)
16,850 GPM (1.05 SpG)
10.37 WT % SOLIDS
8,862,000 LB/HR
1.05 SpG
16,880 GPM
10.0 WT % SOLIDS
(FLOW/UNIT)
F-5-A,B,C
RECIRCULATION
TANKS (3 REQD)
28'Ø×15'
J-1-A,B,C
705 BHP
16,880 GPM } EA.
/HR (TOTAL)
(1.05 SpG)
% SOLIDS
J-4
129 BHP
4,015 GPM
(FLOW/UNIT)
1,462,000 LB/HR GAS
384,400 ACFM
251 LB/HR SOLIDS
(0.09 GRAINS/SCF)
13.5 PSIA
120°F
148°F
280°F
250°F
13.3 PSIA
STACK
GAS
REHEATERS
C-2-D,E,F
48.15 MM BTU/HR
220,000 FT² } EA.
9'×13' DUCTS (3)
14.8 PSIA
J-2-D,E,F
FLUE GAS
BOOSTER FANS
2350 BHP
(INCREMENTAL)
525,400 ACFM } EACH
180°F
148°F
310°F
177°F
14.0 PSIA
STACK
GAS
COOLERS
C-1-D,E,F
48.15 MM BTU/HR
220,000 FT² } EACH
117°F
E-1-D,E,F
SCRUBBERS
TCA CONTACTOR (UOP)
15'×34' LENGTH×40' HIGH
(FLOW/UNIT)
1,448,000 LB/HR GAS
397,200 ACFM
25,167 LB/HR SOLIDS
120°F
8,862,000 LB/HR
16,880 GPM
1.05 SpG
10 WT %
SOLIDS
F-5-D,E,F
RECIRCULATION
TANKS
28'Ø×15'
J-1-D,E,F
705 BHP
16,880 GPM } EACH
729
GPM
896,100 LB/HR (TOTAL)
1794 GPM, 1.0 SpG
RAW
MAKE-UP
WATER
J-6
50 BHP
1975 GPM

1-EQUIPMENT SHOWN WITHIN DASHED LINES NOT INCLUDED IN PROCESS ESTIMATE, (EXCEPT L-1-A,B)

2-INCREMENTAL POND AREA REQUIRED FOR 10 YEAR STORAGE OF LIMESTONE REACTION PRODUCTS IS 2,050 ACRE-FEET.

ISSUE DATE 3-29-71

5	GENERAL	5-21-71	W.B.	
4	CHANGED TO SINGLE STAGE	3-29-71	W.B.	A.G.S.
3	GENERAL	3-25-71	W.B.	L.J.S.
2	ADD NOMENCLATURE	3-16-71	W.B.	L.J.S.
1	ADD QUANTITIES	2-9-71	W.B.	L.J.S.

REVISIONS

SCALE NONE
DRAWN
CHECKED L.J. SCOTTI
APPROVED
DATED 1-27-71
ISSUED FOR FABRICATION
ISSUED FOR CONSTRUCTION

THE M. W. KELLOGG COMPANY
a division of Pullman Incorporated
STEAM POWER PLANT SULFUR
OXIDE CONTROL
WET LIMESTONE PROCESS
NEW 1000 MEGAWATT INSTALLATION

PLANT & ITEM	AREA	JOB NUMBER	DRAWING NUMBER
		4092-50	PD-108-D

DRY LIMESTONE INJECTION PROCESS

A. PROCESS SECTION

1. Process Description (see MWK Dwg. No. PD-107-D)

The dry limestone injection process involves the removal of SO_2 from stack gas by vapor-phase reactions which occur at high temperatures (~2000°F) in the boiler. The following overall reactions describe the calcination and subsequent sulfation steps:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + SO_2 + 1/2\ O_2 \rightarrow CaSO_4$$

The chemistry and kinetics of the process are discussed in more detail in the Chemistry Section of this write-up.

Limestone rock from a nearby quarry is transported by truck, unloaded into a receiving hopper and conveyed to the storage silo, which has been sized for 60 hours limestone capacity. The raw stone is then conveyed to a surge hopper and fed to a pulverizer (Ring-roll mill or Ball mill), where it is mixed with 610°F air for drying and classification. The air-limestone mixture is transported to a feed tank where the air is separated and vented through a bag filter. The solids are fed to a flow splitter vessel containing six outlet nozzles provided with orifice plates. Injection air is supplied to each of the six outlet lines by individual compressors. The air-limestone mixture will be injected into the boiler through six wall-mounted nozzles. The nozzles should be tiltable to vary the angle of injection and should be located at several elevations. These design features are necessary as different limestones will have different optimum injection temperatures.

The boiler stack gas downstream of the air preheater will contain fly ash, unreacted limestone, and the solid reaction products (CaO, $CaSO_4$). This gas (300°F) will be fed to a mechanical separator to remove the bulk of the entrained solids. The design proposed for this separator is a multiple cyclone collector, consisting of about 1,100 - 10 inch diameter cyclone separators mounted in a tube sheet in a single rectangular housing. The gas from the mechanical separator will be ducted directly into an electrostatic precipitator wherein the design stack gas fly ash emission limit must be achieved. This unit will be about 3.0 times the size of a standard precipitator sized for fly ash removal only, because of the lower particle drift velocity and collection efficiency in the presence of limestone additive. The precipitator outlet gas is sent to the stack via an induced draft fan.

The fly ash-limestone reaction product mixture collected in the mechanical and electrostatic separators is conveyed either mechanically or pneumatically to a central sump, wherein it is mixed with sluice water. The solids mixture is then transported to the disposal pond as a 12 wt % solids slurry. It is proposed to recycle the pond overflow water to avoid contamination of adjacent streams with sulfates and sulfites. Make-up process water is added to the sump to compensate for pond evaporation losses and required water of hydration of CaO and $CaSO_4$.

2. Design Bases

The Kellogg flowsheet developed for the dry limestone injection process is for a 350 megawatt installation. This size limitation was established mainly as a judgment factor considering problems inherent in the process of achieving satisfactory limestone distribution and reaction across a large boiler section. Such problems have been quite evident in the TVA full-scale limestone injection tests at Shawnee Unit No. 10(1)*which is rated at 175 megawatts but generally run at lower capacity. To date, the Shawnee tests have not been able

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*** Refers to references at end of section**

to achieve the same degree of CaO utilization when operating at conditions similar to pilot plant reactor tests, presumably due to problems of flow distribution and dead-burning. It does not seem justifiable to propose use of the dry limestone injection process in a new 1,000-MW installation considering its present state of development.

The following tabulation gives the specific process and equipment design bases incorporated in the Kellogg evaluation:

a. Process Design Bases

(1) 350 MW Power Plant assumed as largest feasible size for Dry Limestone Injection process. Use single Boiler and single Air Preheater, single Stack.

(2) 100% Sulfur in coal evolves in Stack Gas as $SO_2 + SO_3$. 71.6% Ash in coal evolves as Fly Ash.

(3) Thermal Deficit due to Boiler reactions involving Limestone and SO_2 is 26.04 MM Btu/hr.
Equivalent Coal Firing Rate = 2,174 lbs/hr
(0.83% of power plant feed rate).

(4) Limestone composition: 91.8 wt % $CaCO_3$ (dry basis)
10.0 wt % moisture

(5) Limestone addition rate = 200% Stoichiometric
100% Conversion of $CaCO_3$ to CaO in Boiler
25% Conversion of CaO to $CaSO_4$ in Boiler
Maximum SO_2 Removal = 50%

b. Equipment Design Bases

(1) Limestone Feed System (TVA Design Bases)
Unloading Hopper; 90 tons capacity (3 hr supply)
Storage Silo; 1800 tons capacity (60 hr supply)
Surge Bin; 240 tons capacity (8 hr supply)
Pulverizer Use Ring-roll mill or Ball Mill
Limestone Feed Rate = 30 tons/hr
Design for 99% minus 325 mesh (44μ)

(2) Boiler Injection System (TVA Design Bases)

Classifying Air = 0.052 lbs/lb Limestone
(vented thru Bag Filter)
Injection Air = 0.475 lbs/lb Limestone

Use Flow Splitter Tank with 6 outlet nozzles equipped with orifices to distribute limestone to 6 boiler injection points.

Injection air added downstream of Flow Splitter by individual Compressors (6). Air injection velocity = 300 ft/sec through tiltable nozzles.

(3) Stack Gas Dust Removal System

Maintain TVA design emission level of 0.10 grains/SCF. Required overall solids removal efficiency is 99.22 wt %.

Specify Mechanical - Electrostatic Collector combination.

Mechanical Collector:

Specify multiple cyclone design with approx. 1,100 - 10 inch diameter tubes in single rectangular housing.

Use cyclone efficiency of 71% per TVA design - assume same particle size distribution as Fly Ash without additive.

Inlet Dust Loading = 13.2 grains/SCF
Outlet Dust Loading = 3.82 grains/SCF
Collector Design $\Delta P \simeq$ 3.5 inches H_2O

Electrostatic Precipitator:

Design Efficiency = 97.33% (higher than TVA design of 96.1% because of higher Ash Coal in current design, i.e., 15.2% vs. 12%).

Inlet Dust Loading = 3.82 grains/SCF
Outlet Dust Loading = 0.10 grains/SCF
Design ESP size = 3.1 x Standard ESP size
required for Fly Ash only
Design Gas residence time = 7.2 seconds
Design Gas velocity = 6.5 ft/sec

(4) Solids Disposal System (TVA Design Bases)

12 wt % solids concentration in sluice water lines to disposal pond.

Pond evaporation loss = 217,000 lbs/hr water

Process make-up water = evaporation loss + water of hydration ($CaO \rightarrow Ca(OH)_2$ and $CaSO_4 \rightarrow CaSO_4 \cdot 2H_2O$)

Incremental disposal pond area of 105 Acre-ft/year to be developed to handle the additional solids resulting from limestone reaction products.

Pond overflow water must be recycled to Sluice Sump to avoid water contamination from sulfates.

3. Design Rationale

In this section, a more detailed discussion is given to support the reasons behind the specific process and equipment design bases incorporated into the Kellogg dry limestone process evaluation. The discussion is sub-divided into the various systems of the process flow sheet.

a. Limestone Feed System

The design bases for the limestone feed system were taken directly from the TVA conceptual design study (2). Suggested improvements on this system have already been outlined in the Kellogg evaluation of the wet limestone scrubbing process. The main criticism is that 60 hours limestone storage seems inadequate for a large installation, and an on-site storage pile with mechanical conveying equipment would appear more desirable. However, this alternate design basis would increase the process investment, and consequently was not included.

The TVA design basis for limestone particle size reduction (70% minus 200 mesh) was increased to 99% minus 325 mesh. This change was made to achieve 25% CaO utilization in the boiler based on pilot plant studies which show increased conversion at reduced particle sizes. The TVA study states that size reduction to 99% minus 325 mesh is still feasible with a ring-roll mill or ball mill. The TVA design bases were used for specifying drying air and injection air rates. The drying air quantity is very low, capable of evaporating only 5% of the water in the raw limestone feed. A much better system would appear to be to use the proper amount of drying air in the pulverizer for complete vaporization, and vent this larger air flow to the boiler rather than to atmosphere.

b. Boiler Injection System

The raw limestone injection rate was set at 200% stoichiometric in this process evaluation. This is consistent with the TVA design basis, and also represents the maximum feasible additive rate consistent with the greatly increased solids handling requirements of the dust collection system. The 200% stoichiometric injection rate combined with a 25% maximum CaO utilization yields a design SO_2 removal of only 50%, which is an inherent limitation of the dry limestone process.

To achieve a higher overall SO_2 removal would involve use of still higher additive injection rates. In addition to increased solids handling problems, this would raise questions of effects on boiler operability; e.g., increased slagging or deposition tendencies, increased erosion of convection-pass tubes, effects on burner firing patterns. None of these possible adverse effects were factored into the present evaluation. There is however, a net thermal deficit due to boiler reactions involving limestone. This deficit is 26.04 million Btu/hr in the 350-MW design case, and the equivalent additional coal firing rate (2,174 lbs/hr) is included in the process utility requirements.

c. Dust Collection System

A mechanical-electrostatic collector combination was specified to maintain the design stack gas solids emission level used in the TVA study, viz, 0.10 grains/SCF. The required overall solids removal efficiency to meet this level with 200% limestone injection is 99.22 weight percent. After consultation with vendors, a mechanical separator design involving use of multiple cyclone collector tubes was selected as the optimum unit to precede a precipitator. Vendor designs were obtained for the specific dust loadings involved, however the TVA mechanical separator design efficiency of 71 wt % was used rather than higher values (75-85%) claimed by vendors. This allows some design safety factor deemed necessary since the actual particle size distribution is not known for the fly ash-reaction products mixture.

The electrostatic precipitator (ESP) design basis was essentially the same as used by the TVA which resulted in an ESP size 2.8 x the standard ESP required for fly ash removal alone. The current design involves higher solids loadings because of the greater ash content of the coal; i.e., 15.2% Ash versus 12.0% Ash in TVA design. The increased loading was factored into the ESP collection efficiency equation using the same particle drift velocity as the TVA design case with additive. This procedure resulted in an ESP size for the current 350-MW design case of 3.1 x the standard ESP unit.

d. Solids Disposal System

The design basis for the solids disposal system was also taken directly from the TVA study and a 12 wt % solids slurry concentration in the lines to the disposal pond was specified. There are some questions of operability and potential plugging with this system due to hydration of reaction products (CaO, $CaSO_4$). The TVA design assumed the pond overflow water could be sent to an adjacent watercourse; however, the current design includes the cost of a recycle system to avoid the question of water pollution. The best answers to questions associated with the solids disposal system should be obtained from full-scale tests at Shawnee.

4. Process Appraisal

The dry limestone injection process is one of the more advanced SO_2 control processes in that it has undergone extensive laboratory and pilot plant studies over the past five years, and is currently being subjected to full-scale boiler tests. Unfortunately, the results of dry limestone process tests have been discouraging, in that 50% SO_2 removal is the best attainable under optimized conditions in a standard pulverized coal-fired boiler. Extensive evaluation of pilot test results by TVA and more recently by Kellogg has shown that 20-25% CaO utilization is the maximum obtainable with the residence time restrictions (2.0 seconds maximum) in a standard B&W or C-E boiler. Attempts to achieve higher than 50% SO_2 removal with this restriction would involve the use of unreasonable limestone addition rates (>200% stoichiometric). It could be possible to realize 90% SO_2 removal at higher gas residence times attainable with a fluid-bed boiler design. This would represent a major development in boiler design practice which is considered beyond the scope of the present evaluation.

The applicability of the dry limestone injection process would appear to be limited to power plant situations wherein 50% SO_2 removal, combined with stack height and atmospheric conditions, would be able to meet local ground-level SO_2 concentration standards. This would appear to limit the process attractiveness to smaller units, either new installations or retrofits (assuming availability of space). The TVA full-scale tests at Shawnee have uncovered a number of potentially serious operating problems which must be overcome. The problem areas are cited below with possible areas for further study indicated.

(a) Limestone Injection

A major limitation of the process is the ability to achieve uniform limestone distribution across the entire cross-section of a large boiler. This problem has been experienced at Shawnee in the 175-MW boiler tests. As a point of reference, the TVA design study for a 200-MW unit would require a boiler cross-section of 24 ft x 58 ft at the burner level. Performance data are being obtained at Shawnee on the effect of injection velocity and injection angle which should be useful. In addition, APCO is funding simulator studies of the air-solids injection system. It is Kellogg's judgment at the present state of development, that the dry limestone process should be restricted to a 350-MW maximum boiler capacity. This conclusion is not applicable for a wet limestone process installation wherein lower CaO conversions in boiler can be compensated for by higher conversions in the scrubbing system.

(b) Boiler Operability

There are several potential questions concerning the effect of limestone injection into the fire box on boiler performance. One problem area is the effect of the additional solids on the stability of the burner firing pattern. Much difficulty has been experienced in the control of the boiler system at Shawnee, which may have been aggravated during periods of limestone addition.

Another major problem area experienced during initial tests at Shawnee is the build-up of reaction products on reheater or superheat tubes. There seems to be wide variation in the extent of this problem experienced at various installations involved in limestone injection tests. Babcock and Wilcox have studied the various factors that would control deposition, e.g., ash fusion temperature, viscosity, sintering strength. Their final report (3) unfortunately, contains only the most general conclusions and does not provide quantitative correlations for predicting limestone-coal ash deposition tendencies. The implication presumably is that any particular coal ash-additive combination being contemplated must actually be studied in the field.

(c) Dust Collection

It is apparent that one of the major cost penalties incurred with the dry limestone injection process will be the substantially larger ESP unit required, i.e., 3.1 x standard ESP for present design. There is much scatter in available information on the effect of limestone additive on dust resistivity, particle migration velocity and collection efficiency. Early tests on an older

REFERENCES

(1) J. T. Reese, TVA Quarterly Progress Report, October-December 1970, Dry Limestone Injection Project 2438 (February 19, 1971).

(2) "Sulfur Oxide Removal From Power Plant Stack Gas - Sorption by Limestone or Dry Lime Process", TVA Conceptual Design Study (1968).

(3) R. C. Attig and P. Sedor, "Additive Injection For Sulfur Dioxide Control - A Pilot Plant Study", The Babcock and Wilcox Company, Research Center Report No. 5460 (March 27, 1970).

(4) TVA Results Report No. 62 - "Electrostatic Fly Ash Collector Performance With Limestone Injection, Shawnee Steam Plant Unit No. 10 Precipitator A", (June 9-July 15, 1970).

(5) A. B. Walker and R. F. Brown, "Effects of Boiler Flue Gas Desulfurization - Dry Additives on the Design of Particulate Emission Control Systems", Dry Limestone Injection Process Symposium (June 22-25, 1970).

(6) J. P. Carey and R. G. Ramsdell, Jr., "Ravenswood Conversion to Coal", Vol. 29, Proc. Amer. Power Conference, 495 (1967).

ESP unit at Detroit Edison showed a severe decrease in efficiency with additive (80% → 55%), corresponding to a factor of 3.7 x base ESP size (2). B&W pilot plant test results (3) predict an ESP size increase with limestone of 2.5 x base case. Recent TVA tests carried out at Shawnee Unit #10 show an average decrease in ESP efficiency of only ten percentage points (4) (92% → 82%). This would represent an increase in ESP size to 1.5 x base case; however there are considerable scatter in the Shawnee test data.

It has been reported (5) that there is a critical dust resistivity of 10^{10} ohm-cm above which the migration velocity decreases rapidly and the ESP collection efficiency decreases. It has been further postulated that resistivity is strongly influenced by the free SO_3 concentration in stack gas, and this level is reduced to virtually zero in the presence of excess CaO from limestone calcination. One suggested means of controlling the resistivity value is through the use of gas "conditioners"; e.g., SO_3, NH_3. There has been some successful experience involving this technique, and it appears worthy of investigation.

Another approach to achieving high ESP efficiency in the presence of additive is to take advantage of the lowered resistivity at higher operating temperatures (>300°F). Con Ed's Ravenswood plant has demonstrated that better than 99% efficiency can be realized by running a "hot" (750°F) ESP unit (6). Such an installation would require breaking into the boiler casing after the superheater with new ductwork to the ESP. This alternate deserves serious study as the cost of the additional ductwork may well be less than a larger ESP unit.

REFERENCES

(1) J. T. Reese, TVA Quarterly Progress Report, October-December 1970, Dry Limestone Injection Project 2438 (February 19, 1971).

(2) "Sulfur Oxide Removal From Power Plant Stack Gas - Sorption by Limestone or Dry Lime Process", TVA Conceptual Design Study (1968).

(3) R. C. Attig and P. Sedor, "Additive Injection For Sulfur Dioxide Control - A Pilot Plant Study", The Babcock and Wilcox Company, Research Center Report No. 5460 (March 27, 1970).

(4) TVA Results Report No. 62 - "Electrostatic Fly Ash Collector Performance With Limestone Injection, Shawnee Steam Plant Unit No. 10 Precipitator A", (June 9-July 15, 1970).

(5) A. B. Walker and R. F. Brown, "Effects of Boiler Flue Gas Desulfurization - Dry Additives on the Design of Particulate Emission Control Systems", Dry Limestone Injection Process Symposium (June 22-25, 1970).

(6) J. P. Carey and R. G. Ramsdell, Jr., "Ravenswood Conversion to Coal", Vol. 29, Proc. Amer. Power Conference, 495 (1967).

DRY LIMESTONE INJECTION

B. CHEMISTRY

1. Qualitative Process Description

As normally conceived the limestone injection process involves addition of calcium carbonate (limestone) or a mixture of calcium and magnesium carbonates (dolomite) at a point where the temperature is high enough to decompose carbonates and form oxides. During a very few seconds of co-current travel with the stack gas the solid oxide particles react with SO_2 and oxygen to form calcium (or magnesium) sulfate. Depending upon the point of addition of the limestone and other reaction conditions there may also be formation of calcium sulfide and calcium sulfite. The solid products are removed along with fly ash and unreacted additives by an electrostatic precipitator or other dust remover.

Chemical reactions between the lime and fly ash components - like silica - decrease the availability of the additive. Incomplete decomposition of the carbonates or recombination of CO_2 with the oxide in a lower temperature zone also lowers the oxide availability. Probably the most serious interference with the course of the reaction, however, comes from the reaction products themselves. As calcium sulfate is formed on the surface of the lime particle it creates a layer through which SO_2 and oxygen must diffuse to the "decreasing core". Generally, because of these and other factors, the actual lime utilization seldom exceeds 30%.

2. Equilibrium Considerations

A Battelle study (1) has examined the chemical thermodynamics of the various species present in the dry limestone process. Several conclusions can be reached on the basis of this examination.

1. High temperatures favor the dissociation of sulfates and sulfites such that CaO is incapable of removing any SO_2 from a typical flue gas above 2250°F and MgO is incapable of removing SO_2 above 1550°F.
2. The tendency of SO_2 to react with CaO to form $CaSO_3$ is completely overshadowed by the much more favorable equilibrium, in the presence of oxygen, with $CaSO_4$. The equilibrium constant for the oxidation of $CaSO_3$ to $CaSO_4$ over the temperature range of interest exceeds 10^5.
3. With CaO at unit activity (pure solid) it is possible to remove all but 1 ppm of SO_2 from flue gas at 1770°F. CaO in solid solution will leave somewhat more SO_2 but the difference would probably not be large. Lower temperatures are, naturally, even more favorable from an equilibrium standpoint.

4. With MgO at unit activity the partial pressure of SO_2 is equivalent to 1 ppm at 1200°F.
5. Limestone theoretically converts to CaO in boiler atmospheres at about 1415°F; at lower temperatures CO_2 in the flue gas will tend to reconvert CaO to $CaCO_3$.
6. On an equilibrium basis, competition between SO_2 and CO_2 for reaction with CaO favors the SO_2 reaction. Theoretically uncalcined limestone should be capable of desulfurizing flue gas since $CaCO_3$ can be in equilibrium with well under 1 ppm SO_2 at 1400°F.
7. This competition between SO_2 and silica from the fly ash is somewhat less favorable in that 0.14 to 3.0 ppm SO_2 exist in equilibrium with a mixture of calcium sulfate and silica or silicates at 1400°F. At higher temperatures, say 1800°F, the equilibrium is shifted such that no SO_2 removal can be expected by calcium silicates.

In summary, there seems to be no significant equilibrium limitations to reacting SO_2 with limestone in a flue gas atmosphere if the temperature is kept below about 2000°F.

3. Kinetic Considerations

The rate of reaction of SO_2 and oxygen with solid calcium or magnesium oxide particles under conditions existing in the hot zone may be limited by mass transfer through the gas film or by the chemical reactivity of the particle.

Mass transfer characteristics may be altered by using a different size particle or changing the gas and particle velocities but there is very little room for maneuvering in these directions. If mass transfer limits limestone utilization to about 30% or less (as has been estimated in theoretical calculations) the only hope for improvement would be to use something like a fluidized bed to increase the residence time of the particle.

The chemical reactivity of the particle is affected by a large number of parameters, of which the two most important are temperature and sulfate loading. Kinetic studies by Borgwardt (2) and Coutant (3) show a severe inhibiting effect due to sulfate loading that appears to limit the limestone utilization obtainable in a few seconds residence time to 20% or less. Increasing temperature has been shown to increase limestone utilization up to the point where back reaction due to decomposition of calcium sulfate becomes important (about 2100°F) but, even here, a 20 to 25% utilization seems to be the most that can be achieved. Again the only hope of achieving higher conversions is by greatly increasing solids residence time.

There are many ways of achieving even less utilization. "Dead burning" of the lime by injection at a point where the temperature is too high - like the firebox - is well known as a cause for decreased reactivity. The high temperatures cause a sintering of the surface resulting in greatly decreased porosity and surface area. At the other extreme, incomplete calcination has been shown to be a cause of decreased reactivity when the temperature is below 1600°F even though the equilibrium is very favorable. Precalcination has been shown to exhibit a negative effect on reaction rate when carried out for an extended time period (2) and when carried out in 0.3 seconds (3). It has recently been argued, on theoretical grounds, that precalcination at relatively low temperatures in the presence of steam and use at low temperatures where some $Ca(OH)_2$ might exist should aid the reaction kientics (4). It is hard to see how this technique would avoid the inhibitory effect of sulfate loading.

Summarizing, the kinetics of the reaction involved in the dry limestone process are too slow to permit efficient utilization without means of providing extra residence time for the solids.

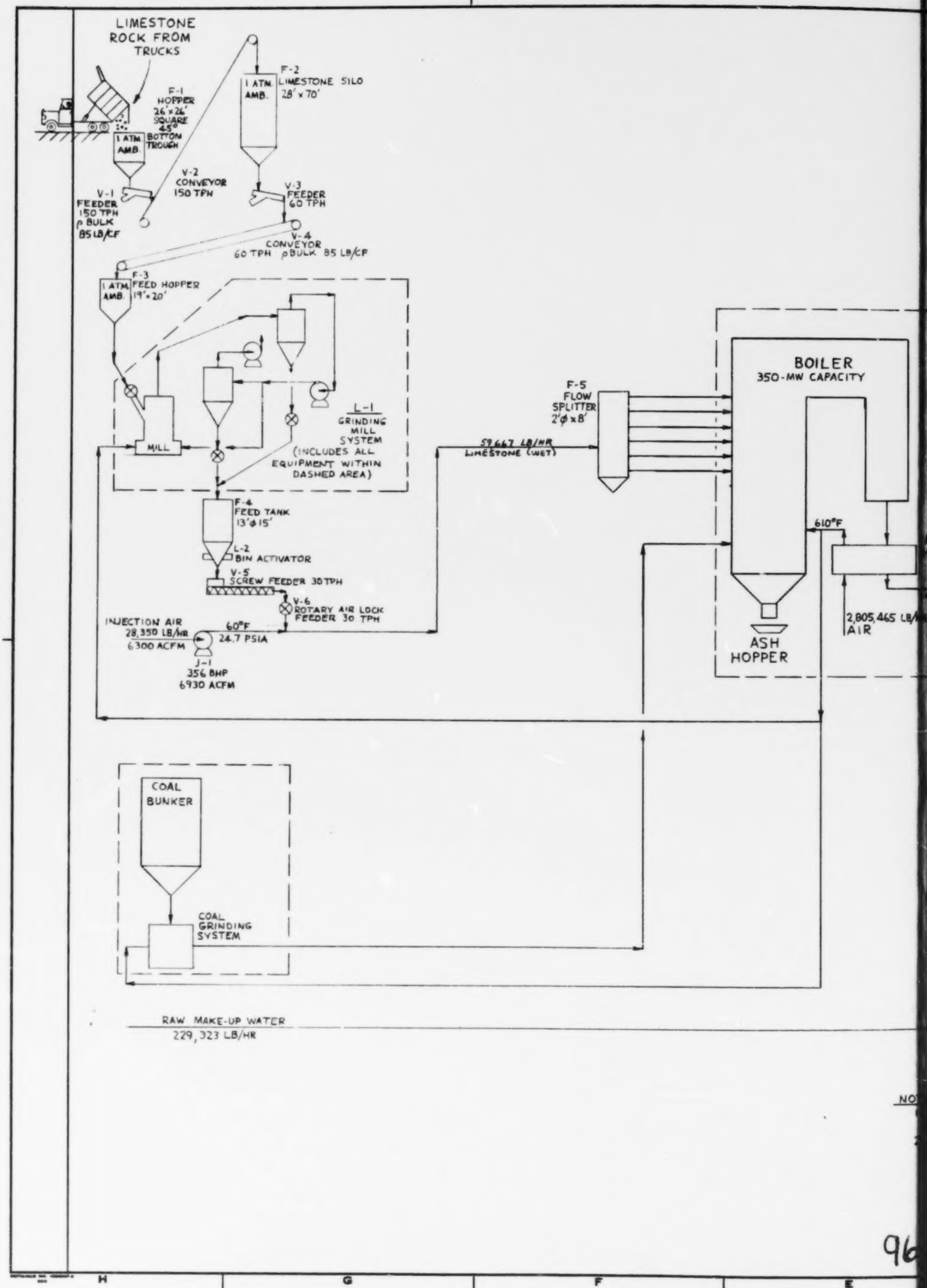
REFERENCES

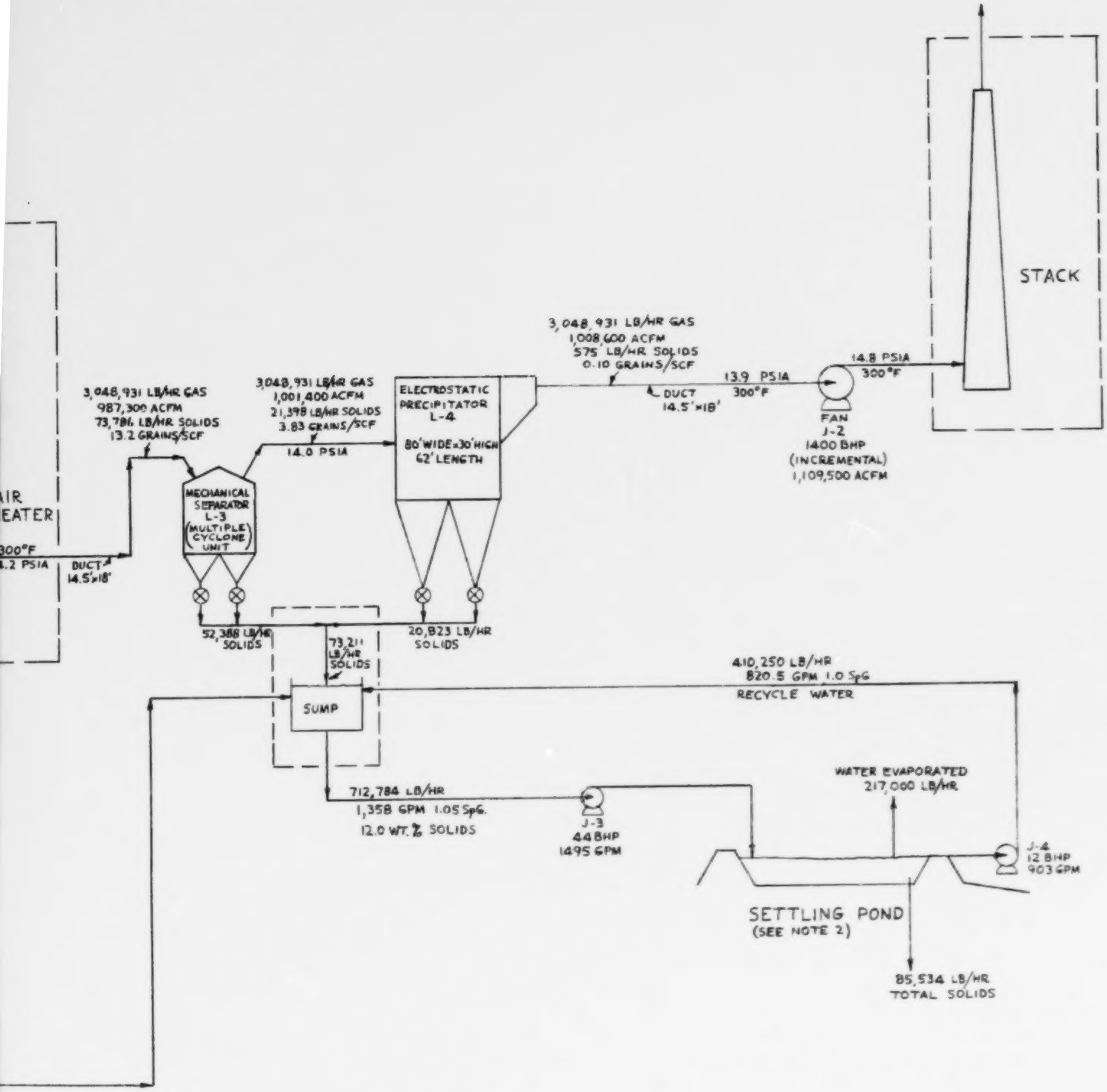
(1) Final Report on Fundamental Study of Sulfur Fixation by Lime and Magnesia by Battelle Memorial Institute, Contract No. PH86-66-108, June 30, 1966.

(2) Borgwardt, Robert H., Environmental Science and Technology, 4, 59 (1970).

(3) Coutant, R.W.; Barrett, R.E.; Simon, R; Cambell, B.E.; and Lougher, E.H.; Summary Report on Investigation of the Reactivity of Limestone and Dolomite for Capturing SO_2 from Flue Gas, Contract No. PH86-67-115, November 20, 1970.

(4) Meyer, Beat and Carlson, C., The Reaction of SO_2 with Metal Oxides, paper presented at the Conference of the American Institute of Chemical Engineers, Chicago, 1970.


LIMESTONE ROCK FROM TRUCKS
F-1 HOPPER 26'×26' SQUARE 45° BOTTOM TROUGH
1 ATM. AMB.
V-1 FEEDER 150 TPH ρ BULK 85 LB/CF
V-2 CONVEYOR 150 TPH
F-2 LIMESTONE SILO 28'×70'
1 ATM. AMB.
V-3 FEEDER 60 TPH
V-4 CONVEYOR 60 TPH ρBULK 85 LB/CF
F-3 FEED HOPPER 19'×20'
1 ATM. AMB.
MILL
L-1 GRINDING MILL SYSTEM (INCLUDES ALL EQUIPMENT WITHIN DASHED AREA)
F-4 FEED TANK 13'ϕ 15'
L-2 BIN ACTIVATOR
V-5 SCREW FEEDER 30TPH
V-6 ROTARY AIR LOCK FEEDER 30 TPH
INJECTION AIR 28,350 LB/HR 6300 ACFM
60°F 24.7 PSIA
J-1 356 BHP 6930 ACFM
59,667 LB/HR LIMESTONE (WET)
F-5 FLOW SPLITTER 2'ϕ×8'
BOILER 350-MW CAPACITY
610°F
2,805,465 LB/HR AIR
ASH HOPPER
COAL BUNKER
COAL GRINDING SYSTEM
RAW MAKE-UP WATER 229,323 LB/HR
H
G
F
E


STACK
IR
EATER
300°F
.2 PSIA
DUCT
14.5'×18'
3,048,931 LB/HR GAS
987,300 ACFM
73,781 LB/HR SOLIDS
13.2 GRAINS/SCF
MECHANICAL SEPARATOR L-3 (MULTIPLE CYCLONE UNIT)
3,048,931 LB/HR GAS
1,001,400 ACFM
21,398 LB/HR SOLIDS
3.83 GRAINS/SCF
14.0 PSIA
ELECTROSTATIC PRECIPITATOR L-4
80' WIDE × 30' HIGH
62' LENGTH
3,048,931 LB/HR GAS
1,008,600 ACFM
575 LB/HR SOLIDS
0.10 GRAINS/SCF
DUCT
14.5'×18'
13.9 PSIA
300°F
FAN
J-2
1400 BHP
(INCREMENTAL)
1,109,500 ACFM
14.8 PSIA
300°F
52,388 LB/HR SOLIDS
73,211 LB/HR SOLIDS
20,823 LB/HR SOLIDS
SUMP
410,250 LB/HR
820.5 GPM 1.0 SpG
RECYCLE WATER
712,784 LB/HR
1,358 GPM 1.05 SpG.
12.0 WT. % SOLIDS
J-3
44 BHP
1495 GPM
WATER EVAPORATED
217,000 LB/HR
J-4
12 BHP
903 GPM
SETTLING POND
(SEE NOTE 2)
85,534 LB/HR
TOTAL SOLIDS

ES
EQUIPMENT SHOWN WITHIN DASHED LINES, (EXCEPT L-1), NOT INCLUDED IN
PROCESS ESTIMATE (SUPPLIED BY POWER PLANT)
INCREMENTAL POND AREA REQUIRED FOR 10-YEAR STORAGE OF
LIMESTONE REACTION PRODUCTS IS 1,050 ACRE-FT.

A

ISSUE① 4-15-71

NO.	DESCRIPTION	DATE	BY	CHECKED
2	GENERAL	5-21-71	W. B.	
1	ADDED NOMENCLATURE	4-15-71	W. B.	

REVISIONS

SCALE: ——
DRAWN: Black
CHECKED: L. J. SCOTTI
APPROVED:
DATED: 1-28-71
ISSUED FOR FABRICATION
ISSUED FOR CONSTRUCTION

THE M. W. KELLOGG COMPANY
a division of PULLMAN INCORPORATED
STEAM POWER PLANT SULFUR
OXIDE CONTROL
DRY LIMESTONE PROCESS
NEW 350 MEGAWATT INSTALLATION

CLASS & ITEM	AREA	JOB NUMBER	DRAWING NUMBER
		4092-50	PD-107-D

DRAWING NO.

THE MONSANTO CAT-OX PROCESS

A. PROCESS

1. Process Description (See MWK Dwg No. PD-100-D)

The Monsanto Cat-Ox Process removes SO_2 from flue gases by catalytically oxidizing the SO_2 to SO_3. The SO_3 combines with H_2O and is condensed and recovered in an absorber using circulating sulfuric acid.

Flue gas leaving the boiler is passed to an Electrostatic Precipitator where >99.5% of the fly ash is removed. The precipitator runs "hot" as the gas to the converter is set at 900°F to achieve the 90% conversion to SO_3 at a reasonable space velocity. The catalyst used is V_2O_5. There is little or no temperature change across the converter. Gases leaving the converter flow to an Economizer where they are cooled by exchange against boiler feed water, and thence to an Air Preheater where they are cooled further by exchange against combustion air. The outlet flue gas temperature is held to 450°F to avoid condensation of sulfuric acid and subsequent corrosion of the Preheater elements.

Flue gas leaving the Preheater is ducted to an Absorber where sulfuric acid vapor is condensed from the flue gas by contact with cold sulfuric acid in a packed bed. Product acid after being cooled to 200°F with recirculating acid is further cooled to 100°F before being sent to storage. Flue gas, together with entrained acid droplets or mist, leave the Absorber at 225°F and enter a Brink Mist Eliminator where most of the entering acid is recovered. Gases leaving the Brink Mist Eliminator are routed to the stack via an induced draft fan.

The circulating sulfuric acid is heated from 200°F to 270°F while contacting the hot flue gas and condensing acid vapor. It has been found economical to recover this low level heat by exchange against combustion air and boiler feed water even though some thermal efficiency is lost through the use of an intermediate recirculating heat transfer fluid. The intermediate fluid system is felt to be necessary to avoid the possibility of sulfuric acid leaking into other systems.

Fine fly ash particles which were not caught by the electrostatic precipitator or the converter appear either in the product acid or in the Mist Eliminator. When the build-up of pressure drop because of entrained fly ash becomes intolerable the Mist Eliminator can be back-washed with acid while on stream.

2. Design Basis

The following conditions were established by Monsanto and used in this study:

Converter Temperature	900°F
Flue gas from Economizer	650°F
Flue gas from Air Preheater	450°F
Flue gas from Absorber	225°F
Acid Circulation Temperature	200/270°F
Acid Product Storage	100°F
SO_2 Conversion	90%
Absorber Packing	2" Intalox Saddles
Absorber ΔP	0.5" H_2O/foot
Flue Gas-Air Exchanger ΔP	5" H_2O

The following design parameters were set by MWK to establish a uniform basis for comparison:

Flue gas velocity in ducts	60 FPS
Motor drive for pumps & fans	
Fan efficiency	70%
Pump efficiency	85%

3. Process Design Rationale

The Electrostatic Precipitator, Converter and Brink Mist Eliminator are proprietary equipment items and will not be discussed. However, it should be mentioned that the Precipitator runs about twice the absolute temperature as is customary and will therefore have to handle twice the gas volume. This, together with the need to design for a higher temperature, per se, plus the higher efficiency needed should result in a much greater than average cost for this item.

Except for the Absorber, the remaining major equipment items are heat exchangers of one type or another. Obviously the temperature differences will directly affect the size of this equipment, but in no case are all the terminal temperatures specified. A number of judgments and assumptions therefore had to be made in sizing this equipment.

C-1 Economizer

In this item, 900°F flue gas is exchanged against boiler feed water. To establish the BFW flow and temperature level it was assumed that the plant had an overall water rate of 5.5 #/KW, that the steam pressure was approximately 2400 PSIG and, because of the high flue gas heat level, that the Economizer heated the BFW close to its saturation temperature. The inlet BFW temperature was backed out from duty, flow and outlet temperature.

Based on the above the Economizer is as follows:

Duty = 606,000,000 Btu/hr
Flue Gas = 8,656,000 #/hr, 900 → 650°F
BFW = 5,500,000 #/hr 650 ← 586°F
Transfer Rate = 9 finned
Surface = 500,000 SF finned = 40,000 SF bare
Use 4 parallel sections each 25' high by 40' wide by 3' deep

Ducts leaving converter based on 60 FPS are 2 at 25' x 25'.
Pressure drop on flue gas side = 4" H_2O

Acid Cooling System

Heat pick-up by acid is fixed by the specified temperatures of flue gas in and out of the absorber. The acid cooling range is also specified (by Monsanto) so the flow quantity can be directly calculated.

As mentioned earlier the heat pick-up in the acid is recovered by exchange with combustion air and BFW, both through an intermediate fluid. There are a number of parameters which must be set before this system can be sized, among them being:

1) The heat transfer fluid used.
2) The combination of flow quantity and temperature range through which the circulating fluid is exchanged. A large flow quantity will lower temperature spreads and reduce exchanger size at the expense of piping and pumping costs.
3) The Δ T split between acid-fluid exchanger and fluid BFW/Air exchanger.
4) The duty split between combustion air preheat and BFW preheat.
5) Combustion air temperature and BFW temperature.

It is obvious that the above parameters can be varied in an almost infinite number of combinations. What follows is one scheme which might be used based on a judgment of reasonable exchanger size, circulating flow rates and temperature approaches.

1) The circulating fluid used is water.
2) Combustion air and BFW were assumed to be available at 80°F and 100°F respectively.
3) Minimum combustion air temperature to Air Preheater to prevent condensation of acid = 350°F.

C-5 Primary Acid Cooler

Duty	176,000,000 Btu/hr
Acid	270 → 249°F
Water	210 ← 170
MTD	69°F
Rate	60 Btu/hr - SF - °F
Surface	42,500 SF
Number of Sections	- 48 arranged 4 series x 12 parallel 8" x 13'
Type	Teflon

C-6 Secondary Acid Cooler

Duty	414,000,000 Btu/hr
Acid	249 → 200°F
Water	209 ← 140
MTD	50
Rate	60
Surface	138,000 SF
Number of Sections	- 150 8" x 13'
Type	Teflon

Teflon is used here because it is known to be suitable for this service. The obvious drawback is in the large number of sections required. Perhaps for an application of this magnitude Du Pont would develop a larger bundle size so that fewer sections would be required--the present maximum bundle size is 8" x 13' long. Aside from the high cost of manifolding lies the difficult control problem associated with such large numbers of parallel sections. Not studied were alternate materials which could be fabricated into a fewer number of larger sections although this should definitely be part of a complete study.

C-7 BFW Heater

The quantity of BFW flowing to the Economizer was assumed to be available here at 100°F.

Duty	414,000,000 Btu/hr
Water	209 → 140
BFW	175 ← 100
MTD	37
Rate	300
Surface	37,300 SF
Sections	4- 42" x 30' Tubes
Mat'l	TP 410 tube side
ΔP	10 to 15 psi each side

C-4 Combustion Air Primary Heater

Duty	176,000,000 Btu/hr
Water	210 → 170
Air	170 ← 80
MTD	61.7
Rate	8
Surface	350,000 SF finned
Size	28' high by 40' wide by 3' deep

C-3 Combustion Air Steam Heater

Assume 300 psig steam available.

Duty	377,000,000 Btu/hr
Steam	422 → 422
Air	350 ← 170
MTD	144
Rate	7.2
Surface	340,000 SF + 20% for cold air condition
Surface	408,000 SF
Size	28' high x 40' wide x 3' deep

Air Preheater

Duty	485,000,000 Btu/hr
Flue Gas	650 → 450°F
Air	550 ← 350

A Ljungstrom regenerative type preheater should be used here because of relatively low cost. The air leakage inherent in this design is not reflected by the above temperatures.

Acid Product Cooler

Duty	4,100,000 Btu/hr
Acid	200 → 100
Cooling Water	100 ← 85
MTD	36
Rate	55
Surface	2100 SF
Size	3 @ 700 SF

Absorber

A Monsanto study in which 2.5 MM SCFM of flue gas were handled resulted in 9 towers of 30' Ø with 16' beds packed with 2" Intalox saddles. Proration of the above based on flue gas quantity for both pressure drop and heat transfer would result in 4- 40' towers of 24' bed depth. A check of this size using the generalized pressure drop correlation would suggest that it is a little tight. For this reason, as well as the unusually large diameter and bed depth, 8 towers are suggested of 30' Ø with 20' bed depths.

Number of towers	8
Tower size	30' Ø x 41'
Packed Bed	20' - 2" Intalox Saddles
Pressure Drop	10" H_2O
Material	Carbon steel lead lined plus acid resisting brick

Pumps

Acid Circulating Pump

80% Sulfuric Acid - Worthite (cast steel)
23,000 GPM - Say 6 @ 4000 GPM
50 psi differential

$$\text{BHP} = \frac{23{,}000 \times 50}{1715} = 670$$

Driver - Motor 6 @ 150 HP

Circulating Water Pumps

BFW - Acid
Water - 12,000 GPM
40 psi differential
BHP = 280
Driver - Motor - 350 HP

Combustion Air - acid
Water - 8800 GPM
40 psig differential
BHP = 205
Driver - Motor - 250 HP

Fans

Combustion Air - Forced Draft

Capacity	8,150,000 #/hr - 1,680,000 SCFM
Static Pressure	10" Water (Δ due to SO_2 removal)
Temperature	0 to 100°F
Type	Centrifugal - 4 parallel
Drive - Motor	2830 BHP @ 70% Eff - 4000 HP = 4 @ 1000 HP

Flue Gas - Induced Draft

Capacity 8,650,000 #/hr
1,750,000 SCFM
Static Pressure 29" Water (Δ due to SO_2 removal)
Temperature - 225°F
Type Centrifugal - Minimum 2 parallel
Drive - Motor HP = 11,100 BHP @ 70% Eff = 16,000 HP
= 4 @ 4000 HP

F-1 High Level Circulating Water Drum
8800 GPM @ 3 minute holding time
Use 2-9' Ø x 28' Drums

F-2 Low Level Circulating Water Drum
12,000 GPM @ 3 minute holding time
Use 2-10' ID x 30' Drums

F-3 (A-P) Product Acid Storage Tanks (16 Req'd)
Basis: 104 GPM @ 30 days
Capacity Required = 5,000,000 Gal.

4. Process Appraisal

General

As suggested in the chemistry review, this process is severely handicapped by the need of a high reaction temperature. The volume of flue gas handled by the Precipitator and Reactor are twice the volume of the same weight flow at more normal convection section exit temperatures. Also the frictional pressure drop through the system will be higher because of the higher temperature. A catalyst which would permit operation at 450°F would avoid a redesign of the boiler (i.e., external economizer) and probably result in a better air preheat system because of the flexibility in processing sequence. This should prove particularly advantageous in add-on applications where a reheat system is now required.

As pointed out in other evaluations, the market for the product acid is quite variable. Also, a successful process which depends on product sales to appear economically attractive is self-defeating because the product will be in over-supply.

Flow Distribution

The large volumes of flue gas and combustion air being handled will probably give rise to distribution problems. These problems should arise not only where one line or duct divides into two or more but may cause trouble in heat transfer equipment and the induced draft fans where fairly uniform velocity profiles are essential for proper operation. Perforated distribution plates will probably be required in the former and straightening vanes in the latter.

Because of the large diameter absorbers and deep beds, attention to distribution of both gas and liquid is critical for satisfactory performance in this equipment.

Fuel Flexibility

The sulfur content of the fuel used in this study is approximately 3.5%. However, it should be remembered by prospective users of this process that throughput will have to be reduced for higher sulfur content fuel if emission standards are to be met. For example, the combustion of the design quantity of 5% S coal will result in about 85% conversion as compared to 90% at the lower SO_2 loading. This will result in an SO_2 stack gas concentration of about 2.2 times the design value. In addition, the Air Preheater would probably suffer corrosion due to the higher dew point of the acid.

Operation at lower sulfur levels than design does not appear to be a problem except for the loss of "product".

Fly Ash Removal

Problems associated with fly ash comprise plugging of the catalyst beds, plugging of the mist eliminators, and contamination of the product acid. The rate at which the catalyst beds are plugged depends on the amount of dust in the entering flue gas which in turn depends on the efficiency of the electrostatic precipitator and the ash content of the coal burned in the power plant. When the catalyst bed becomes plugged to the extent that pressure drop becomes excessive and/or conversion falls off, the catalyst must be cleaned. This requires shutting down the unit, cooling the catalyst, removing and cleaning the catalyst, and recharging the unit. This operation likely will require several days. Catalyst loss owing to attrition and breakage will, of course, be a direct operating expense.

The dust not removed either in the precipitator or the absorber ultimately will appear in the product acid--either directly or indirectly from back washing the mist eliminators. The effect of this fly ash on product acid marketability and selling price is unknown. No provisions for filtering the product acid have been included.

Owing to the need for very high dust removal, the precipitator must be maintained in good working order at all times. This will probably give rise to higher than normal maintenance costs. No provisions for recovering from an outright precipitator failure have been included.

EQUIPMENT LIST

C-1 A,B,C,D	Economizer
C-2 A,B,C,D	Air Preheater
C-3 A,B,C,D	Combustion Air-Steam Heater
C-4 A,B,C,D	Combustion Air-Circulating Water Heater
C-5	Primary Acid-Circulating Water Cooler (48 sections)
C-6	Secondary Acid-Circulating Water Cooler (150 sections)
C-7 A,B,C,D	Boiler Feed-Circulating Water Exchanger
C-8 A,B,C	Product Acid Cooler
D-1 A,B,C,D	Converter
E-1 A-H	Absorber
F-1 A,B,	High Level Circulating Water Drum
F-2 A,B	Low Level Circulating Water Drum
F-3 A-P	Product Acid Storage Tank
J-1 A-H+2 spares	Circulating Acid Pump & Drive
J-2 A,B+spare	High Level Circulating Water Pump & Drive
J-3 A,B+spare	Low Level Circulating Water Pump & Drive
J-4 A,B,C,D	Combustion Air Fan & Drive
J-5 A,B,C,D	Flue Gas Fan & Drive
J-6	Product Acid Pump
J-6A	Spare
L-1A-H	Brink Mist Eliminator
L-2 A,B	Precipitator

B. CHEMISTRY

In the Monsanto Cat-Ox Process, SO_2 is oxidized in the gas phase through the catalysis by V_2O_5:

$$SO_2 + 1/2\ O_2 \overset{V_2O_5}{\rightleftharpoons} SO_3$$

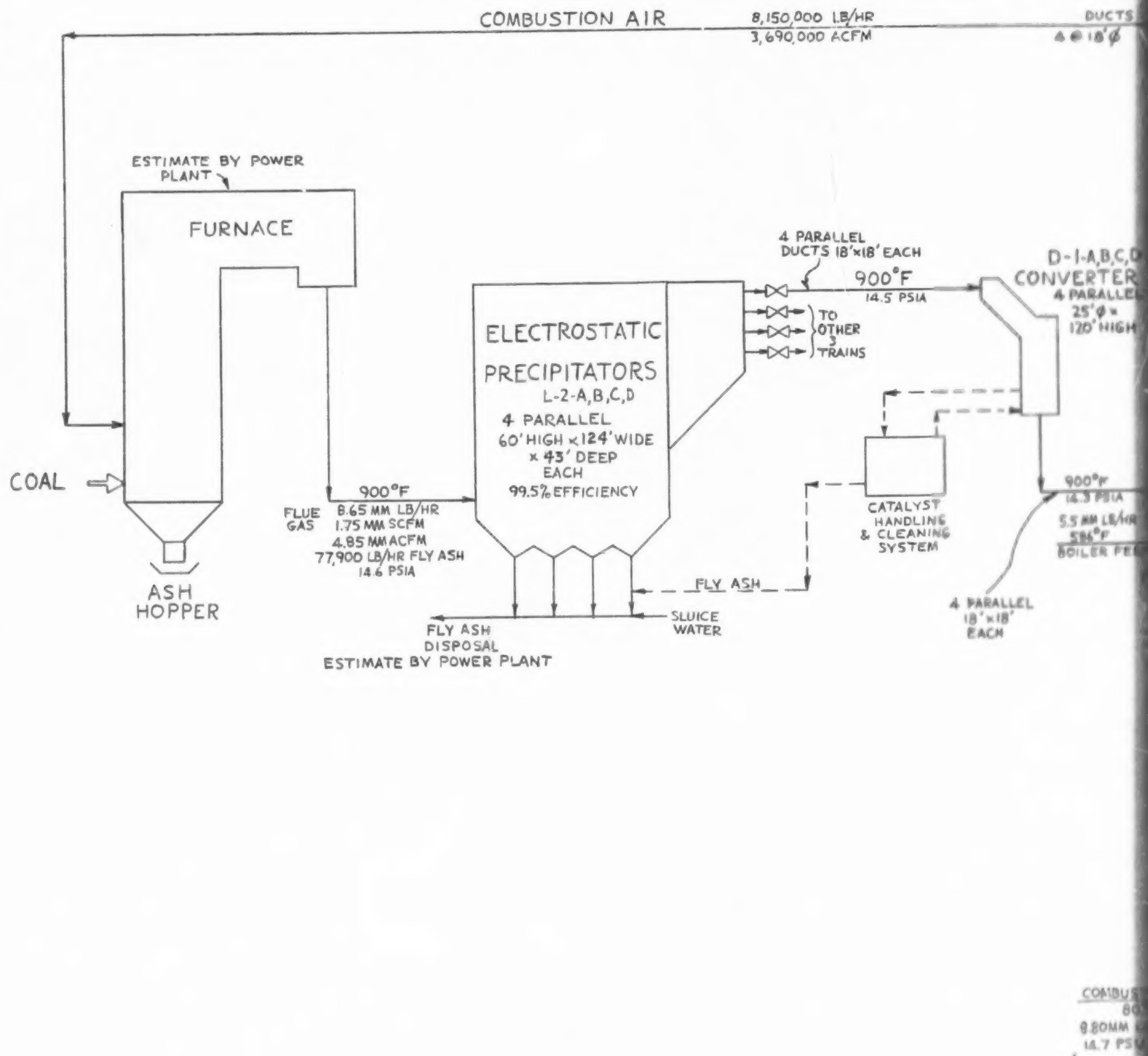
According to the equilibrium data, SO_2 conversion is favored by low temperature. But the reaction rate is favored by high temperature. Therefore, the Cat-Ox has operated at about 900°F at the catalytic converter inlet, giving about 90% conversion of SO_2 in the stack gas. The conversion is limited by the equilibrium constant which is controlled by the partial pressure of SO_2 and oxygen.

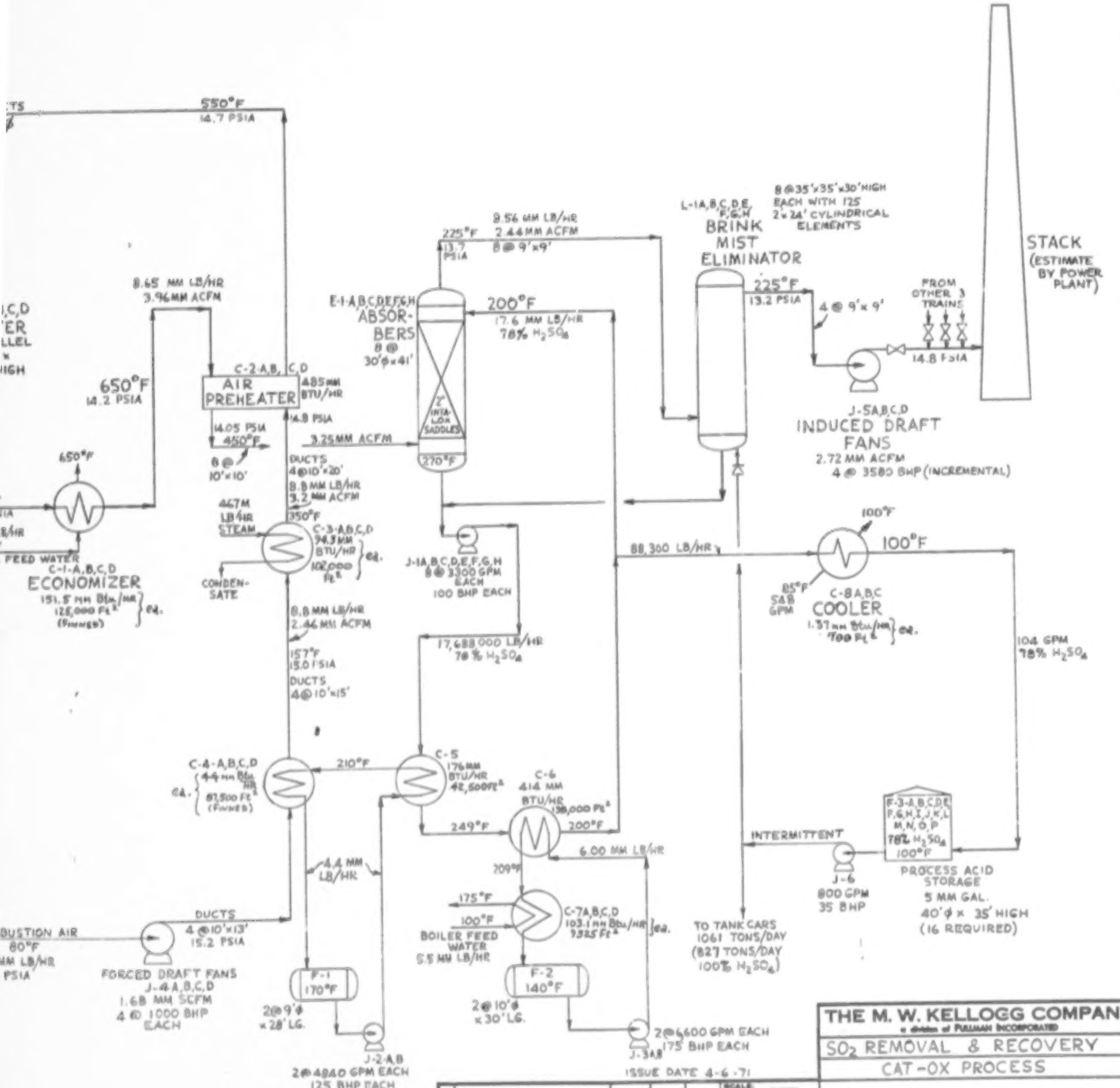
Although the reaction appears simple, there has been much controversy about the mechanism of the catalysis by V_2O_5. The question of the mechanism remains unsettled because only the deductive approach of the Hougen-Watson type has been used in the kinetics studies. Recently, some workers have considered that changes in valence of the vanadium is part of the mechanism. This is based partly on the idea that potassium salt as a catalyst promoter exists as a liquid phase that dissolves V_2O_5. However, so far, no direct physical measurement such as electron spin resonance has been made.

Vanadium pentoxide catalysts generally contain 7 to 9% V_2O_5 and K/V ratio of from 2 to 4 on a siliceous carrier. They require a temperature above about 750°F to be effective. The Cat-Ox process is said to use a specially designed catalyst which prevents poisoning by ash components.

An absorption tower is used to condense the sulfuric acid. The very fine sulfuric acid mist particles are removed from the flue gas stream with a Brink Mist Eliminator. Flue gas which has passed through the Brink Mist Eliminator contains less than 1.0 milligrams of 100% H_2SO_4/SCF, which means that the stack gas contains less than 10 ppm of 100% H_2SO_4 as a mist. The vapor pressure of sulfuric acid at 225°F will contribute another 11 ppm of 100% H_2SO_4 so that the total sulfuric acid loading in the exit stack gas is about 20 ppm. The inlet gas in the absorption tower contains about 4000 ppm of SO_3. Therefore, the over-all efficiency of the absorption tower and the Mist Eliminator for the sulfuric acid removal is 99.8%.

The sulfuric acid produced has an acid concentration of about 80%.


COMBUSTION AIR
8,150,000 LB/HR
3,690,000 ACFM
DUCTS
4 @ 18'ϕ
ESTIMATE BY POWER PLANT
FURNACE
COAL
ASH HOPPER
900°F
FLUE GAS
8.65 MM LB/HR
1.75 MM SCFM
4.85 MM ACFM
77,900 LB/HR FLY ASH
14.6 PSIA
ELECTROSTATIC PRECIPITATORS
L-2-A,B,C,D
4 PARALLEL
60' HIGH × 124' WIDE × 43' DEEP EACH
99.5% EFFICIENCY
FLY ASH DISPOSAL
ESTIMATE BY POWER PLANT
SLUICE WATER
FLY ASH
4 PARALLEL DUCTS 18'×18' EACH
900°F
14.5 PSIA
TO OTHER 3 TRAINS
D-1-A,B,C,D
CONVERTER
4 PARALLE
25'ϕ ×
120' HIGH
CATALYST HANDLING & CLEANING SYSTEM
900°F
14.3 PSIA
5.5 MM LB/HR
586°F
BOILER FE
4 PARALLEL 18'×18' EACH
COMBUS
80
9.80MM
14.7 PSI


CTS
550°F
14.7 PSIA
8.65 MM LB/HR
3.96MM ACFM
,C,D
ER
LLEL
HIGH
650°F
14.2 PSIA
C-2-A,B, C,D
AIR PREHEATER
485MM BTU/HR
14.8 PSIA
14.05 PSIA
450°F
8 @ 10'×10'
650°F
FEED WATER
C-1-A,B,C,D
ECONOMIZER
151.5 MM Btu/HR
125,000 Ft²
(FINNED)
ea.
DUCTS
4@10'×20'
8.8MM LB/HR
3.2 MM ACFM
467M LB/HR STEAM
350°F
C-3-A,B,C,D
94.3MM BTU/HR
102,000 Ft²
ea.
CONDEN-SATE
8.8MM LB/HR
2.46 MM ACFM
157°F
15.0 PSIA
DUCTS
4@10'×15'
E-1-A,B,C,D,E,F,G,H
ABSORBERS
8 @ 30'φ×41'
2" INTALOX SADDLES
270°F
3.25MM ACFM
225°F
13.7 PSIA
9.56 MM LB/HR
2.44MM ACFM
8@9'×9'
200°F
17.6 MM LB/HR
78% H₂SO₄
J-1A,B,C,D,E,F,G,H
8@3300 GPM EACH
100 BHP EACH
17,688,000 LB/HR
78% H₂SO₄
L-1A,B,C,D,E,F,G,H
BRINK MIST ELIMINATOR
8@35'×35'×30' HIGH EACH WITH 125 2'×24' CYLINDRICAL ELEMENTS
225°F
13.2 PSIA
4@9'×9'
FROM OTHER 3 TRAINS
14.8 PSIA
STACK
(ESTIMATE BY POWER PLANT)
J-5A,B,C,D
INDUCED DRAFT FANS
2.72 MM ACFM
4@3580 BHP (INCREMENTAL)
88,300 LB/HR
100°F
100°F
85°F
548 GPM
C-8A,B,C
COOLER
1.37 MM Btu/HR
700 Ft²
ea.
104 GPM
78% H₂SO₄
C-4-A,B,C,D
44 MM Btu/HR
87,500 Ft²
(FINNED)
ea.
210°F
C-5
176MM BTU/HR
42,500Ft²
C-6
414 MM BTU/HR
138,000 Ft²
249°F
200°F
6.00 MM LB/HR
209°F
4.4 MM LB/HR
175°F
100°F
BOILER FEED WATER
5.5 MM LB/HR
C-7A,B,C,D
103.1 MM Btu/HR
9325 Ft²
ea.
F-1
170°F
2@9'φ × 28' LG.
F-2
140°F
2@10'φ × 30' LG.
J-2-A,B
2@4840 GPM EACH
125 BHP EACH
J-3A,B
2@6600 GPM EACH
175 BHP EACH
DUCTS
4@10'×13'
15.2 PSIA
BUSTION AIR
80°F
MM LB/HR
PSIA
FORCED DRAFT FANS
J-4A,B,C,D
1.68 MM SCFM
4@1000 BHP EACH
TO TANK CARS
1061 TONS/DAY
(827 TONS/DAY 100% H₂SO₄)
INTERMITTENT
J-6
800 GPM
35 BHP
F-3-A,B,C,D,E,F,G,H,I,J,K,L,M,N,O,P
78% H₂SO₄
100°F
PROCESS ACID STORAGE
5 MM GAL.
40'φ × 35' HIGH
(16 REQUIRED)

ISSUE DATE 4-6-71

THE M. W. KELLOGG COMPANY
a division of PULLMAN INCORPORATED

SO_2 REMOVAL & RECOVERY
CAT-OX PROCESS

NO.	DESCRIPTION	DATE	BY	CHKD
7	CHG. AREA C-5, C-6	8-11-71	TMW	
6	CHG. CAP. J-1,2,3,6	5-13-71	W.B.	
5	ADDED PRESSURES	5-11-71	W.B.	
4	ADDED SOME QUANTITIES	4-6-71	W.B.	
3	GENERAL	4-1-71	W.B.	
2	ADD DATA ON L-1	3-29-71	W.B.	
1	GENERAL	3-26-71	W.B.	

REVISIONS

SCALE: ——
DRAWN:
CHECKED:
APPROVED:
DATED: 2-3-71
ISSUED FOR FABRICATION
ISSUED FOR CONSTRUCTION

CLASS & ITEM	AREA	JOB NUMBER	DRAWING NUMBER
		4092-50	PD-100-D

DRAWING NO.

MOLTEN CARBONATE PROCESS

A. PROCESS

1. Process Description (See MWK Dwg No. PD-124-D)

The Molten Carbonate Process for removal of SO_x from power plant flue gases was initially conceived and developed by Atomics International who have done extensive research and development studies. The firm of Singmaster and Breyer, of New York City, have further developed the process and have proposed a design*, still in preliminary form, for the application of the process to an 800 megawatt power plant burning coal with three percent sulfur content.

To bring the information in the Singmaster and Breyer report to a common basis with studies being made on other sulfur removal processes, their original equipment sizing has been modified as required. Except for the correction of obvious errors, the Singmaster and Breyer design bases have been retained in nearly every instance. The major exceptions are: 1) the gas velocity in the absorber towers has been reduced to avoid excessive entrainment, and 2) a quench step has been introduced ahead of the Claus plant.

Drawing #PD-124-D shows a conceptual scheme for the molten carbon process required for a 1000 MW power plant burning coal containing 3.5% W sulfur. A P&I flow sheet was not made for our process evaluation, but its concept can be seen on Drawing PS-218-0002 in the Singmaster and Breyer report.

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* "An Evaluation of the Atomics International Molten Carbonate Process", prepared for NAPCA by Singmaster and Breyer, Contract CPA 70-76, November 30, 1970.

The process consists of scrubbing of flue gas at 850°F with a molten eutectic mixture of lithium, potassium and sodium carbonates (minimum melting point 750°F). The melt, containing sulfite and sulfate salts, is regenerated by heating to 1500°F, where the sulfates formed by disproportionation of the sulfites can be reduced to sulfides with carbon. The sulfides in the melt are converted back to carbonates with the formation of hydrogen sulfide by reaction at 850-950°F with carbon dioxide and steam. The regenerated melt is circulated to the flue gas scrubber and the H_2S evolved is sent to a Claus plant for the recovery of elemental sulfur.

Fly ash entering the scrubber with the flue gas is picked up by the circulating melt and must be removed by filtration. The filtration process entails a loss of melt with the filter cake. Most of the lithium salts so lost are recovered, but the sodium and potassium salts are discarded with the fly ash; therefore, the fly ash quantity entering the absorber must be minimized. Consequently, a minimum efficiency of 99.5% is required for the power plant electrostatic precipitator and further, the precipitator has to be relocated such that it processes flue gas at 850°F rather than the usual temperature of 300°F.

2. Basis for Material Balances

a. Flue gas specifications

Flue gas quantity	293,000 moles/hr
Fly ash	77,900 lbs/hr
Flue gas composition -	mole fraction
SO_2	0.00261
SO_3	0.00005
CO_2	0.13657
N_2	0.74085
O_2	0.03276
H_2O	0.08714
HCl	0.00002

Chloride composition of flue gas must be considered since reaction will occur with K_2CO_3 to form KCl which must be rejected from the process to minimize its build-up. The amount of K_2CO_3 consumed is related to the chloride content of coal.

b. Precipitator

99.5% W fly ash removal from 850°F flue gas

c. Absorber

	% Absorbed	Moles Absorbed / mole M_2CO_3 melt
SO_2	95.0	0.1435
SO_3	94.0	0.0160
HCl	95.0	0.0018
O_2	1.0	0.0337
Total	-	0.1950

The absorber material balances have been prorated from Singmaster and Breyer's report and as a somewhat different flue gas analysis is now used, are not in 100% balance.

d. Reduction

Coke and combustion air are supplied in sufficient quantity to maintain the reduction reaction at 1500°F with complete consumption of carbon and oxygen and 95% reduction of M_2SO_4 by carbon. All of the N_2 and enough of CO_2 to maintain an 85% stoichiometric excess of CO_2 in the regenerator are vented to the stream of scrubbed flue gas returning to the power plant. It is assumed that 95% of the sulfur in the coke is converted to M_2S with the remainder retained in the solid residue. Metals, ash and unburned coke, totaling 4% of the dry coke feed are contained in the reducer effluent melt and are removed by filtration.

For heat and material balance purposes, the 12% volatile combustible matter (VCM) in the coke is assumed to flow from the reducer with the exit CO_2 gas, 86% passing to the regenerator and 14% to the power plant. This assumption may not be valid, since at 1500°F in the presence of oxygen, the VCM of the coke probably will both burn and crack to H_2, CH_4 and carbon. If this occurs the coke requirement will be reduced by an amount equivalent to the heat released by this combustion.

Although it is clearly stated by Singmaster and Breyer that the green petroleum coke contains 5-8% moisture, they have ignored this in the material balance, which has been made on a moisture-free basis. Revision of this design concept is beyond the scope of this report.

e. General

All melt flow rates for the 1000 MW power plant molten carbonate system were obtained by direct scale-up of melt stream compositions from Singmaster and Breyer's flow sheet PS-218-000. Due to lack of time no attempt was made to calculate material balances based on theory of absorption or reduction or regeneration reactions. Unit material balances were checked however, and all balances on the Singmaster and Breyer flow sheet were verified except around the reducer, where slight discrepancies were observed. Therefore, the reducer balance for the 1000 MW plant has been carried through on "scale-up" basis.

f. Li_2CO_3 Recovery

Pilot plant investigations reported by Atomics International have shown that 88% of the lithium salts lost from the circulating melt with the fly ash and coke filter cakes can be recovered as Li_2CO_3 and re-introduced into the circulating melt as make-up. None of the sodium and potassium salts so lost are recovered in this process.

Carbonate make-up requirements of the 1000 MW plant, on a water-free basis, are:

Lithium Carbonate, net	115 lbs/hr
Sodium Carbonate	990 lbs/hr
Potassium Carbonate	1684 lbs/hr

An equivalent quantity of soluble mixed salts (carbonates, sulfides, sulfites, sulfates and chlorides) are discarded with the fly ash and coke slurry.

g. Claus Plant

Design sulfur recovery by the Claus Plant is 92%, an economical value for a plant charging the type of gas which is produced by the regenerator. The off-gas from the Claus plant is recycled to absorber where the un-recovered sulfur in the gas is picked up by the melt and recycled to attain essentially complete recovery of the sulfur removed from the power plant gas. Only a small quantity of sulfur, about 320 lbs/hr., is lost with the soluble salt slurry as sulfites, sulfides and sulfates.

3. Process Design Rationale

a. Absorber

Atomics International studies of the absorption of SO_x in molten carbonate resulted in a recommendation to use a spray tower for process design. Results from their study showed that the melt circulation rate could not be below that resulting in a minimum M_2CO_3 concentration of 68% at the absorber outlet. This is the lowest practical concentration as set by freezing point consideration. As the melt concentration is increased above this value, a high ratio of $M_2CO_3:SO_x$ entering the absorber results. Recycling of melt from the absorber outlet to the inlet decreases this ratio (the recycle contains up to 32 mol % SO_x). Recycling was recommended to maintain the ratio of liquid-to-gas as high as practical, thus insuring maximum contact of the gas with the liquid. Atomics International have set a $M_2CO_3:SO_x$ ratio as 10:1 maximum, thus limiting the recycle ratio to about 3.

Singmaster & Breyer has recommended that the absorbers be designed for series flow on the liquid side but with parallel flow on the gas side to increase the melt/gas mole ratio and so insure sufficient absorption of SO_2. In addition, M_2CO_3 recycle had been incorporated into the absorber design to obtain a high absorber flow rate with minimized melt circulation through the rest of the process. In the absorber Singmaster & Breyer's design criteria for 95% removal of SO_x from flue gas were based on a superficial gas velocity of 25 ft/sec and a liquid spray mean particle size of 100 microns. However, in our judgment, the superficial gas velocity for the spray tower must be limited to 10 ft/sec in order to avoid excessive entrainment loss.

In this design for a 1000 MW plant a gas velocity of 10 ft/sec necessitates the use of eight spray towers with the flue gas flow in parallel. The liquid flow is four in series through two parallel trains, with the streams combined in common pump tanks after each pair of towers. The recycle flows are individual to each pair of towers, i.e., the bottom liquid from the first towers is returned to the inlets of these towers, etc. The spray towers are specified as being 35 ft in diameter by 34 ft high. The absorber pumps are designed as being capable of a 3:1 recycle ratio. Additional design criteria for vessel sizing, insulation, and materials of construction areas are as specified by Singmaster & Breyer.

b. Fly Ash Filtration

Filtration requirements are as specified by Singmaster and Breyer with scale-up for the 1000 MW power plant. The filter requirements are for 2 units operating alternately, with a 45 min. cycle time per filter. The filter units are leaf type designed for maximum pressure drop of 50 psi at full load, requiring 1350 ft^2 filtration area per unit.

c. Reducers

The main reactions which occur in the reducers are:

Oxidation: $M_2S + 2O_2 \longrightarrow M_2SO_4$
$C + O_2 \longrightarrow CO_2$
Reduction: $M_2SO_4 + 2C \longrightarrow M_2S + 2CO_2$
Disproportionation: $4M_2SO_3 \longrightarrow 3M_2SO_4 + M_2S$
Coke S Recovery: $S + \frac{1}{2}C + M_2CO_3 \longrightarrow M_2S + 3/2\ CO_2$

The endothermic heat for reduction of M_2SO_4 to M_2S, and the sensible heat required to raise the melt, coke, and air to the reduction temperature of 1500°F are provided by the oxidation of M_2S and carbon (coke). At 1500°F, the M_2SO_3 in the melt disproportionates to M_2SO_4 and M_2S.

Four reduction vessels, operating in parallel, have been provided for a 1000 MW power plant facility. Each reducer is a two compartment vessel--one an oxidation zone and the other a reduction zone, with liquid passage between the two compartments for internal melt recirculation. The basic parameters for design of the reducers are:

Liquid Retention Time	20 min.
Static depth of Melt	2-3 ft.
Superficial Gas Velocity	3 FPS
Bed Expansion	100% max.

A further detailed discussion of the basis for reducer vessel design including vessel configuration, selection of insulation and materials of construction can be found in the Singmaster & Breyer Report.

Combustion air for the reducers is preheated by heat exchange with oxidation zone off-gas, and admitted to the oxidation zone of the reducer through sparger pipes. The oxidation zone off-gas is then sent to the power plant boiler with the absorber off-gas. The reduction zone off-gas, consisting essentially of CO_2, is quenched by water and/or steam to reduce the CO_2 gas stream temperature from 1500°F to 850°F and sent to the regeneration. This quench provides the 85% excess steam necessary for the anticipated operation of the regenerator. The quench steam is assumed to be available from the waste heat boiler in the Claus plant. The CO_2 production in the reducer exceeds the regeneration requirements at 85% excess, so the surplus CO_2 is vented to the oxidation zone off-gas stream.

Melt from the reducers is cooled in the reducer quench tank to 950°F by recirculating 850°F reduced melt from the reducer product coolers. This recirculation controls the temperature of the melt in the quench tank.

In the heat and material balances of the reducer S & B assumed that the VCM content of the delayed petroleum coke, which is 12% by weight, merely vaporizes and passes off with the CO_2 gas. This is extremely improbable. In practice, this material, consisting of heavier petroleum hydrocarbons, should be released from the coke almost instantaneously when the coke is brought to 1500°F by contact with the hot melt. There should be immediate reaction with oxides in the melt to convert all the VCM to CO_2 and water. There may be a tendency at this temperature for a water gas equilibrium producing some CO as well.

Singmaster & Breyer's treatment of this VCM as inert is conservative for the reducer design, but puts an undue burden on the regenerator and the Claus plant. If credit were taken for combustion of this VCM, the coke requirement of the unit would be reduced by about 12%.

Moisture in the coke has also been ignored by Singmaster & Breyer. This amounts to 5 to 8% of the dry coke weight. Introduction of this much water vapor in the reducer may promote a water gas reaction resulting in excessive amounts of H_2 and CO in the CO_2. An afterburner in the reducer off-gas line might be required to oxidize these undesirable materials.

d. Coke Filtration

Coke filtration requirements are similar to those for fly ash, but with only 1000 ft^2 filtration area required. Unreacted coke is removed from the process melt and sent to the Li_2CO_3 recovery process. The filtered melt is then sent to the regenerator.

e. Regeneration

The regeneration reaction is expressed as:

$$M_2S+CO_2+H_2O \longrightarrow M_2CO_3+H_2S$$

The regenerator is a tower consisting of 15 bubble cap trays where melt is in countercurrent contact with CO_2 and H_2O. Regeneration is exothermic and coolers are provided with melt recirculation through the tower as shown on the flow sheet. Only one tower is required for the 1000 MW plant facility.

The theoretical number of trays required is approximately 4 based on equimolar quantities of CO_2 and H_2O at an excess of 85% with little or no inert diluents present in the gas. The equivalent tray efficiency is 27%. Justification for this design is discussed in the Singmaster & Breyer report. It is expected that the two zone design of the reducer will minimize the inert diluent gases that can affect the separation.

The flow rate of regeneration gas feed, and therefore the excess of CO_2 in the regenerator, is controlled by venting surplus CO_2 gas from the reducer to the combustion gas stream being returned from the reducer to the power plant.

The regenerator tower is designed for a 15 minute minimum retention time on the trays. With melt recycled for cooling, approximately a 2-inch level is required on the tray, producing a static head loss of 30" for the 15 trays. Since the liquid has a specific gravity of 2.0, this static head is equivalent to a pressure drop of 2.1 psi. There are other tower losses and piping losses as well. With the reducer operating at 6.0 psig, the exit gas from the regenerator will be at approximately atmospheric pressure.

f. Treatment of Regenerator Off-gas

Off-gas from the regenerator, excluding the "coke volatiles", is 34% H_2S and 33% each CO_2 and H_2O, at a temperature of 850°F and one atmosphere pressure. For best operation a Claus plant should have cold gas feed at a pressure of at least 5 psig. High water vapor content greatly increases the cost of the plant, as does high inlet temperature.

Cooling, de-watering and compression of the regenerator off-gas is indicated in order to obtain an optimum design for the Claus plant. A quench tower, with heat removal by water circulation, is a practical means of condensation. This tower, containing four trays and five baffles, receives the 850°F regenerator off-gas which is cooled to 120°F by countercurrent flow of condensate cooled to 110°F and reheated to 160°F, the dew point of the gas, as it flows over the trays and baffles. Most of the water in the regenerator off-gas is condensed by this quench. The 160°F liquid is pumped through an air cooler and its temperature reduced to 110°F and then recirculated to the top of the tower. The net condensate is recycled to the regenerator as quench water for the CO_2 feed gas. Almost half of the total 24,200,000 Btu/hr cooling duty is from condensation at 160°F or lower, with the rest of the duty originating as sensible heat between 850° and 110°, so that no heat recovery is justified.

The cooled gas is compressed to 6 psig by a centrifugal blower, passed through a water-cooled condenser which removes the heat of compression and condenses more water, and flows to the Claus plant at 100°F and 5 psig, conditions which are most economical for the sulfur plant design.

g. Claus Plant

The Claus plant used to recover elemental sulfur from the treated regeneration gas is a conventional unit which is offered competitively by several contractors. The cost of the plant increases with the degree of sulfur recovery. Here a recovery of 92% has been specified since the off-gas is recycled to the absorber and an ultimate recovery of nearly 100% of the absorbed sulfur will be attained. The only sulfur loss will be that in the soluble salts discarded with the fly ash and coke slurry. This loss is estimated to be only 1.3% of the sulfur removed from the flue gas.

It is important that the feed gas to a Claus plant does not contain more than 2% hydrocarbons, and these should be not heavier than propane. Excess hydrocarbons will result in a "black" sulfur product and will upset the heat balance of the unit, resulting in damage from overheating.

It has been assumed that the hydrocarbon content of the net feed (after water removal) will be a maximum of 20 mols/hr (1.3 vol. %). If more hydrocarbon than this is found likely, it will be necessary to remove the VCM from the coke fed to the reducer or to incinerate the VCM in the reducer off-gas.

h. Coke Handling Facilities

Green delayed coke of 2-inch maximum size is delivered in rail cars and fed to a crusher to reduce it to ¼ inch maximum size. The crushed coke is screened and oversize returned in closed circuit to the crusher. The crushed material is charged to 3 coke silos with a total of 3 days live storage capacity. The unloading and crushing facilities are sized for operation of one eight hour shift per day.

From the silos the coke is fed to coke bins associated with each reducer. Coke flows from the coke bins via weigh feeders which measure coke into blow tanks from where it is then charged to the reducers, using air pressure supplied by the combustion air blower.

Detailed equipment layout for the coke material handling equipment may be found in the Singmaster & Breyer report for an 800 MW power plant facility. This equipment has been scaled up directly for the 1000 MW facility, requiring 3 storage silos instead of two to maintain live storage capacity for increased coke consumption requirements.

No provision has been made for removing moisture from the coke. As received this moisture normally may be 5-8% by weight and in bad weather it may be more. Although not specified by Singmaster & Breyer, it would seem advisable to provide a weather roof over the unloading and handling facilities, particularly since this operation must be done daily, handling some 8-50 ton cars per 8-hour day. Excess rain water accumulated in unloading and handling will be detrimental to the process. There is a possibility that drying of the coke before charging to the reducer may be required.

If the plant is in a location subject to freezing weather, special precautions must be made to insure that the coke supply is not interrupted by freezing in the cars or in the unloading equipment.

i. M_2CO_3 Make-up

Carbonate make-up requirements total 43 tons per day, of which about 10 tons is Li_2CO_3 recovered from discarded fly ash and coke filter cakes. Facilities are provided to receive the three carbonates by bulk truck shipment. The salts are dumped into a receiving hopper from which they are transferred by a bucket elevator and cross conveyor to their respective storage silos. The recovered Li_2CO_3 is discharged into the same silo as the fresh. Approximately 4 to 5 days storage is provided, so that the K_2CO_3 hopper is larger than the other two.

From the silos, weigh feeders and conveyors deliver the proper carbonate quantities to the Carbonate Melt Tank. As sized by Singmaster & Breyer, the electric heater capacity of this tank is sufficient to heat and melt the make-up on a continuous basis and to balance radiation loss at 850°F. Only about 25% surge capacity was provided; for the 1000 MW plant the over-capacity has been increased to 40%. The melted carbonate make-up is pumped continuously into the regenerator bottoms pump tank.

This whole make-up system appears to be designed on the basis that all three salts will be received as anhydrous materials. No provision has been made to cope with any water content of the raw materials, and no heater capacity for vaporizing water of crystallization is included.

These salts are deliquescent and must be protected from the atmosphere at all times. Although not specified by Singmaster & Breyer, all carbonate handling facilities must be housed to insure that the fresh salts are kept dry.

For start-up purposes, this carbonate melt tank is essential. However, during routine operation it should be possible to introduce the cold make-up salts directly into the regenerator bottoms pump tank, using a screw conveyor or a standpipe to overcome the 2 psig positive pressure in the tank. There is ample surplus heat here not only to heat and melt the make-up carbonate but also to drive off any water of crystallization which the salts might contain.

j. Li_2CO_3 Recovery Process

Lithium carbonate is a relatively expensive material (42-52¢/lb). Appreciable quantities of melt are discarded with the fly ash and coke filter cakes; the loss of the lithium in these discards would impose a definite economic disadvantage on the process.

The recovery process is based on the insolubility of lithium carbonate and its easy conversion to soluble lithium bicarbonate. Laboratory work to establish the feasibility of the process was done by Atomics International. Singmaster & Breyer's development of the process is far from complete, with some sections apparently in the conceptual stage.

Filter cakes from the fly ash and coke filters at 850°F are dumped periodically and are quenched with water, flowing to the dissolving sump. Here all salts except lithium carbonate are dissolved. Fly ash, coke residue, and lithium carbonate are slurried in the resulting salt solution, then filtered. The filtrate, containing only a small quantity of dissolved lithium salt, is discarded. The filter cake is re-slurried with a circulating stream of water, which contains 0.7% of Li_2CO_3 in solution. This slurry is charged in batches from a receiver to a reactor when it is agitated with inert gas containing 12% CO_2. The carbonate is converted to soluble bicarbonate, leaving the ash and coke residue as slurry which is dumped into a surge tank. Slurry from this surge tank is filtered to remove the fly ash and coke residue, which is discarded. The filtrate is collected and charged batchwise to a reactor where it is blown with hot air to strip out the CO_2 and re-convert the bicarbonate to carbonate. This insoluble carbonate is discharged as a slurry to a surge tank from which it is fed to a filter. The filter cake is passed through a drier and sent to the Li_2CO_3 storage silo. The filtrate containing some dissolved Li_2CO_3, is recycled to slurry the filter cake discharged by the fly ash filter.

Atomics International report successful recovery of 88% of the lithium entering the recovery system. This efficiency has been used as the basis for the present design.

k. Changes to Existing Power Plant

If this process is to be applied to an existing 1000 MW power plant some revisions to the present boilers will be required. It may be assumed that the plant is equipped with an electrical precipitator following the air heater but ahead of the induced draft fans. In all probability the efficiency of this precipitator is not over 99%. In any case, it will not be suitable for operation at 850°F with 99.5% dust collection efficiency so it must be replaced. It is assumed that its dust handling and disposal equipment is in good condition and can be salvaged for use with the new precipitator.

The boiler casing must be modified to allow all the flue gas to exit at a temperature of 850°F, pass through the new precipitators and absorbers and return, still at 850°F, to the economizer section of the boiler. The present precipitator would be removed and the induced draft fans would be replaced to give added capacity equal to the increase in draft loss imposed by the new equipment. This added power requirement resulting from the replacement is 10,000 BHP.

4. Process Appraisal

A brief summary of engineering development efforts required for commercializing the process are summarized below for each step in the process including absorption, filtration, reduction, regeneration, and lithium recovery.

a. Absorption

The main difficulty inherent in commercial design of absorbers which needs to be further demonstrated is the ability to eliminate melt carryover in the absorber off-gas. Melt loss in the absorber off-gas is undesirable from an economic standpoint and intolerable from a corrosion standpoint since melt carried by the scrubbed gases may condense in the return vapor line or in the boiler system. Condensation of melt on the cold surfaces of the boiler would cause rapid decrease in heat transfer and premature shutdown for cleaning.

No investigation has been made on the loss of melt to flue gas by vaporization. The carbonate salts have a low but definite vapor pressure. The flue gas leaving the absorber will be saturated with melt vapor at 850°F. When the gas is cooled to 300° in the economizer and air heater of the power plant, most of this vapor will condense and drop out as dust. Some plating of cold surfaces may occur.

The proposal to operate the absorber at a superficial velocity of 25 ft/sec is outside the scope of known commercial practice. In other processes, velocities well below this are used for particle transport, i.e., 100% entrainment. A maximum velocity of 10 ft/sec is suggested, and even at this lower rate, it is doubted that entrainment can be low enough to permit the use of a demister pad for effective entrainment separation.

In towers of this size (35' diameter), distribution of the inlet gas becomes an important factor. No inlet distributors are indicated by Singmaster & Breyer. It is felt that elaborate turning vanes with a perforated plate distributor above them will be required in the bottom of the absorber tower.

The flue gas duct sizes indicated result in velocities of 106 ft/sec from the precipitator and 156 ft/sec to and from the absorber tower. It is felt that these velocities should be limited to 60 ft/sec to avoid uneconomic pressure drops and difficult flow distribution problems.

There is no assurance whatsoever that the 95% absorption of SO_x obtained by Atomics International in a 4" tower with a single spray can be duplicated in a 35' diameter vessel. The possible corrections for wall effects and other factors are mentioned by Singmaster & Breyer who advise that extensive plant scale studies will be required.

A recycle range of 1:1 to 3:1 on melt circulation through the absorbers has been recommended. However, no provision for adequate distribution of this stream by sprays in the tower has been shown. The operating range of a spray nozzle is extremely limited and best results are obtained only when the flow is held very close to design rate and pressure. It would appear advisable to design and operate the spray system at the maximum recycle pump capacity, particularly since no disadvantage to a high recycle rate has been shown.

The ability to remove fly ash from flue gas by electrostatic precipitation at 99.5% efficiency over extended operating periods is highly questionable and must be demonstrated. The possibility of plugging spray nozzles by ash in the recycle melt increases greatly if actual fly ash removal efficiency is below 99.5%, causing an increase in fly ash concentration in the melt. Correspondingly, continuous spray nozzle operation must be demonstrated for increased ash contents of the melt.

Demister design requires further consideration and demonstration that it will not plug with melt or fly ash, can be operated with acceptable pressure drop and will effectively eliminate carryover.

The fourth and final absorber pump tank is oversize so that it may hold the surges in the melt circulation. Therefore, its instrumentation should be only a Level Recorder, with a Flow Controller on the filter outlet measuring the entire melt circulation and resetting four Flow Ratio Controllers on the feeds to the four reducers.

Flow indicators are needed on the recycle melt streams to each of the absorbers.

b. Fly Ash and Coke Filtration

A complete discussion of commercial design problems associated with filtration may be found in the Singmaster & Breyer report. Suitability of pressure leaf filters as selected by Singmaster & Breyer for cost estimation must be verified with prototype tests. The calculation of filter area requirements for the 1000 MW plant facility uses empirical relationships developed by Atomics International.

These correlations must be verified with prototype test data for pressure leaf filters for both fly ash and coke filtrations.

No means of preventing excessive heat loss and possible freezing of the flow in the filters has been suggested. This should be investigated. The alternately off-stream filters must be maintained at 850°F as well.

c. Reduction

Continuing development efforts are required for satisfactory solution and demonstration of the following:

(1) Materials of Construction

The design of a reduction vessel must be verified regarding its structural integrity and ability to withstand corrosive attack.

(2) Reducer Configuration

The two-zone reducer concept has not been physically demonstrated to date and thus requires additional effort to insure operability. The object of the two-zone design is to separate oxidation gases from reduction gases so that reduction gas alone may be used for regeneration. Equipment sizing and configuration for an 800 MW plant facility was investigated by Singmaster & Breyer on an economic basis alone. On a technical basis, it will be important to better define the location of a zone separation baffle and the size of baffle plate openings required to insure proper melt circulation. The dynamics and reliability of melt circulation between the two zones must also be verified.

(3) Reducer Off-Gas Composition

The reducing zone off-gases should contain a minimum of N_2, CO, and hydrocarbons from coke volatiles since the presence of any of these gases in large amounts will affect the operability of the Claus plant. Afterburning of reducing zone off-gases may be required to convert unburned hydrocarbons and CO to CO_2. If excessive unburned hydrocarbons reach the Claus plant, black sulfur will be produced.

(4) Reducer Off-Gas Cooling

Corrosion problems inherent in the design of reducer off-gas cooling relate to the chloride and melt composition of the gas. Melt carryover in the reducer off-gas must be minimized and at 1500°F, chlorides may vaporize from the melt.

(5) Coke Addition

As reported by Singmaster & Breyer, it may be necessary to introduce coke in the form of a slurry with the melt in order to insure coke contact with the melt in the reducer. Also, sufficient agitation with air must be maintained, but is limited by the degree of melt expansion and frothing that can be tolerated.

(6) Coke Distribution

It is obvious that the consumption of coke in the reducing and oxidizing zones must be closely controlled to obtain the desired off-gases and overall reaction. The suggested design does nothing to achieve this distribution. Back circulation of reduced melt is required to bring the required quantity of carbon into the oxidizing zone and to maintain nearly equal temperatures in the two zones. A means of forcing this circulation under proper control should be developed.

Temperature records of both sections of the reactor are necessary so that the coke and combustion air quantities can be adjusted as required. Continuous analysis of the off-gas is needed to keep the coke and air flows in the proper proportions.

The instrumentation shown by S & B is not practical in that the valve shown to release excess CO_2 from the reducing section to the oxidation section exit gas has no pressure drop and if closed will merely result in internal short-circuiting of gas through the circulation ports in the internal baffle. This line should be left open and its flow controlled by regulation of the off-gas rate of the reducer which in turn is regulated by the charge rate of the Claus plant.

As mentioned elsewhere, studies should be made to determine the effect of water introduced with the coke, and if necessary provision for its elimination should be included. Similarly, the effect of the VCM in the coke should be determined and the current design basis modified to reflect the reactions which occur due to its presence. Hydrocarbon material in the CO_2 gas must be eliminated as it cannot be tolerated in the Claus plant in concentration above 2.0%.

d. Regeneration

Regeneration studies would appear to be more thorough than those for some other parts of the process. The proposed design seems feasible, using bubble cap trays to obtain the desired liquid retention while allowing for significant changes in the gas rate as may be expected from the normal load variations of the power plant. These variations, estimated to give a turndown of 50%, would be greater than are practical for the use of perforated trays.

Pressure drop in this tower will be greater than anticipated by the Singmaster & Breyer estimate.

e. Claus Plant

It was assumed by S & B that feed gas at 850°F, and 3" H_2O pressure, containing 32% water vapor would be suitable for feed to a sulfur recovery plant of the Claus type. The conventional feed to such a unit is supplied at 100-120°F under 5 psig pressure, which results in a much more economical installation and more satisfactory operation. Added facilities to cool, de-water and compress the feed gas are specified for the 1000 MW system.

Hydrocarbons in the feed to a sulfur plant are highly undesirable. As previously discussed, it is important that the reducer system be designed in such a manner that hydrocarbon generation is minimal.

Cost of a sulfur plant is influenced by the completeness of the sulfur recovery. In this case the off-gas is to be recycled to attain 100% sulfur yield. A once-through recovery of 92% has been chosen as a suitable design basis. For final design a more complete economic study should be made, considering the incremental cost imposed on the other parts of the system by this recycle and balancing this against the cost of the Claus plant.

f. Raw Material Handling

For a final design the problems which may arise in the handling of the coke and carbonates should receive more attention. Delivery facilities for these materials will be especially designed for each plant and will vary with the source of the various materials. The railroad facilities for eight cars of coke per day will be extensive, requiring trackage for storage of both full and empty cars. The size and arrangement of these facilities will be governed by the dependability of the rail service.

Availability of the carbonates in the required quantities must be known. It is possible that the potassium and sodium carbonates will be available only as hydrates and that the storage system and melt facilities must be designed with this in mind.

g. Lithium Carbonate Recovery

In the Singmaster & Breyer design of the carbonate recovery section there are several areas of uncertainty. These are not insurmountable problems and should be resolved easily for final design.

It is probable that the filter cakes from the fly ash filter and the coke filter will be discharged alternately, and quickly. It would seem advisable for these hot slugs to drop into the dissolving sump where an appreciable mass of water has been accumulated. This will keep a reasonably steady temperature on the feed to the Li_2CO_3-fly ash filter. However, this alternating slug flow should be held in the sump for sufficient time to produce a constant quality feed to the filter. The Singmaster & Breyer sump is not large enough for this. Four to six cycles, or three to four hours holding time would be required. The approximately 54 minutes provided is insufficient.

As specified by S & B the Lithium Carbonate Filtrate Receiver (T-108) and the $LiHCO_3$ Reactor Feed Pump (P-109) are included with the Fly Ash Filter and are duplicates of items associated with the Li_2CO_3-Fly Ash Filter. This cannot be, as the receiver and pump must be designed for batch loading of the Li_2CO_3 reactor (T-108 must be larger, P-109 must be for vacuum suction). This has been corrected in the 1000 MW specifications.

No specifications at all are given for the Hot Air Blower which supplies air to the Li_2CO_3 Reactor. On the basis of chemical equilibrium the reactor should operate as close to 212°F as is practical. Working away from the 25 HP motor size specified by S & B, the air delivered might be 2000 lb/hr. No source is shown for the hot air; it might be assumed that it could be taken from the discharge of one of the air cooled exchangers at perhaps 300°F. If this air were at 300°F, its heat on a 100% efficiency basis would be enough to give only an 8° rise in the water in the reactor. It is clear that this step of the process has not received proper attention.

An inert gas generator is provided to supply gas of about 12% CO_2 content at 75 psig for the $LiHCO_3$ Reactor. Singmaster & Breyer specification for this unit seems to be in error as to the cooling water required by this equipment. For this specified capacity the water use might be 545 GPM rather than 75 GPM stated. The fuel requirement for the 800 MW plant is 8000 SCF/hr (not 8000 SCFM). The space provided on the plot plan for this generator, including a blower driven by a 30 HP motor and a compressor driven by a 200 HP motor, all said to be skid mounted, is but 6'4" x 11'0" (scaled). On the basis of the size of similar units, in other plants, this space is inadequate and the unit is too large for mounting on a single skid.

This generator is specified to deliver gas of 12% CO_2 content. The necessity of the generator is questionable when a practically limitless supply of desulfurized flue gas of higher CO_2 content is available from the stack of the power plant at 300°F. Only the compressor would be required, and this would be located at the stack, delivering the gas at 75 psig through connecting piping.

A dryer is provided for the Li_2CO_3 filter cake recovered by the process. S & B have specified a moisture content of the feed which is eight times the quantity of dry carbonate, but the stated fuel consumption of the drier will evaporate only a fraction of this quantity of water. This amount of water does not appear elsewhere in the material balances, so it may be in error. The design basis for this dryer should be reviewed.

h. Waste Disposal

This process requires the disposal of an appreciable quantity of slurried waste containing dissolved salts. For the 1000 MW plant studied here the slurry discard composition is estimated to be as follows:

Water		15,000 lbs/hr
Air	390	
Coke Residue*	1285	
Total Solids	1675 lbs/hr	
KCl	685	
Mixed Salts**	2157	
Total Dissolved Salts	2842 lbs/hr	
Total		19,517 lbs/hr

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* Includes nickel, iron & vanadium oxide.

** Sulfate, sulfite, sulfide, and carbonate salts of sodium, potassium & lithium

In many locations there will be a disposal problem. Consideration should be given to development of a means of salvaging the salt, particularly the potassium and residual lithium salts which now incur appreciable make-up costs.

The valuable metals in the coke ash may total as much as 0.1 wt. % of the coke, equivalent to 500 to 700 lbs/day of vanadium and nickel. Recovery of these metals might prove profitable.

i. Temperature Maintenance

High quality insulation has been specified for most of the equipment in order to minimize heat loss and avoid "cold spots" which could cause freezing of the melt. Electric heating elements sized to overcome heat losses are included in the pump tanks. It has been assumed that in the case of shutdown all of the melt will be drained into these tanks and maintained at 850°F to prevent freezing. There is no overall pumpout system to rid all of the equipment of melt so that it can be cooled for maintenance.

such an arrangement is advisable. A single large tank would be provided for total melt storage. During any prolonged shutdown the melt could be allowed to cool and freeze and would be re-melted for start-up. Either electrical heating or direct fired flues through the tank could be used.

In the Singmaster & Breyer report all of the melt piping is specified as "electrically traced". This is necessary not only to prevent freezing during operation but to heat the system prior to start-up so that the melt can be circulated. Such electrical heating, whether by resistance or by induction is rather expensive and much electrical gear is required.

No suggestion has been made as to how the regenerator, the coolers, the reducers, and the filters are to be heated prior to start-up to prevent freezing of the melt at the start of circulation. This will require further study and development of operating techniques.

B. CHEMISTRY

1. Literature Reviewed

The following list of reports from Atomics International have been reviewed:

1. Development of a Molten Carbonate Process for Removal of Sulfur Dioxide from Power Plant Stack Gases, 6/1/67 - 2/28/68.
2. Progress Report No. 2, Part 1, Process Chemistry, Reduction, 4/1/68 - 10/27/68.
3. Progress Report No. 2, Part 2, Process Chemistry, Regeneration, 4/1/68 - 10/27/68.
4. Progress Report No. 2, Part 5, Fly Ash Studies, 4/1/68 - 10/27/68.
5. Progress Report No. 3, 10/28/68 to 7/31/69.

In reviewing the chemistry, the process flow will be followed from the absorber to the filter, reducer, regenerator and back to the absorber.

2. Absorber

Although a reasonable number of basic melt properties for the pure eutectic of lithium, sodium and potassium carbonates has been mentioned, additional data should be obtained at or near the actual composition of the steady state absorber fluid. First of all, the pure melt has a melting point of 747°F but with 20% sulfite-sulfate the melting point appears to be about 780°F, thus to operate at 800°F without knowledge of viscosity and the effect of fly ash on this melt may be dangerous. Although, the last report recommended 800 to 850°F, without further knowledge 850 to 880°F looks like a somewhat safer range for operation at this time. It is recommended from the literature that melt viscosities should not exceed 200 centipoises for reasonable flows and we concur with this.

Atomics International indicates that SO_2 absorption is not affected by the level of sulfite-sulfate in the melt up to reasonable quantities, by the presence of 10% fly ash and by the presence of water vapor and/or oxygen in the flue gas. Sulfur dioxide absorption is very rapid, irreversible and apparently gas-film controlled. The reactions of interest in the absorber are:

$$SO_2(g) + M_2CO_3(l) \longrightarrow M_2SO_3(l) + CO_2(g) \quad (1)$$

$$SO_3(g) + M_2CO_3(l) \longrightarrow M_2SO_4(l) + CO_2(g) \quad (2)$$

$$1/2\ O_2(g) + M_2SO_3(l) \longrightarrow M_2SO_4(l) \quad (3)$$

There is no reason to believe that SO_3 will not be taken up by melt although no experimental evidence was noticed. Some study of reaction (3) indicated it was not as fast as reaction (1), but that a substantial amount of the sulfite formed in reaction (1) could be oxidized to sulfate (flue gas contains 3.3% O_2). This is a function of the time of contact of melt and gas, thus dependent on the type of contactor.

Although results showed nitrogen oxide absorption at a slower rate than SO_2 absorption, no identification of the products was mentioned. One might expect that decomposition or reduction to nitrogen gas occurs. However, nitrite-nitrate buildup in the melt should be checked. Experiments were performed which showed that H_2S was not emitted into the flue gas from the melt, at least at the level of 0.4 wt.% sulfide in the melt, despite the presence of water vapor and carbon dioxide in the flue gas. Therefore sulfide level must be low in the absorber to present no problems in this direction.

Some of the experiments performed by AI were done in a bomb type container with gas being bubbled through a few inches of melt. The rate of flow of gas was low, usually well under 0.1 ft/sec superficial gas velocity, whereas good mixing and more conventional flows would require greater than 0.25 ft/sec superficial gas velocity. Naturally at these flows baffling must be done to prevent excessive entrainment or carryover out of the reactor. In other words, the experiments were performed at flow velocities which did not approach practical values and this must be kept in mind. Larger contactor tests were made - wetted wall, baffled tube, spray tower - at superficial gas velocities up to 30 ft/sec. Removal of SO_2 was easily obtained. The results indicated the wetted wall had to be about 9 times as long as the baffled tube to get similar SO_2 removal efficiency. About 5 ft/sec linear velocity in the baffled tube showed 4" of H_2O pressure drop which was considered excessive. Spray tower tests have not been completed. Contactor design does appear to be the major problem for the absorber.

3. Fly Ash Removal

AI has shown that it is preferable to remove the fly ash from the melt coming from the absorber and before going to the reducer. From a temperature standpoint, it is also the lowest melt temperature in the process and may allow the use of a metal filter. The sulfide content is also low which is a desirable condition from corrosion and solubility limitations. At higher tmeperatures fly ash can be significantly attacked by a molten carbonate system and show high solubility of silica.

Enough work appears to be done to fix the composition of the filter cake at roughly 2/3 melt and 1/3 fly ash. However, it was not established whether this tie up of melt was due to just physical absorption or partially to chemical reaction.

The solubility of iron and calcium oxides to the extent of about 0.2 gram metal/100g melt at 840°F is of interest. The formation of a red color due to iron oxide solubility in a 62% M_2CO_3, 37% M_2SO_4 melt may be indicative of ferrite or ferrate formation. For instance, K_2FeO_4 is a deep red in color.

The fact that 25 to 65 micron opening filters can be used to filter out fly ash which contains a large amount of particles less than 25 microns is indicative of melt addition to fly ash to form particles larger in size which do not pass even 65 micron openings.

It is suggested that future filter development include life tests on the material to be used especially under the cycling conditions envisaged for this operation. Naturally, design of the filter requires maintaining equipment in contact with melt above the freezing point of the system especially during potential upset conditions.

4. Reducer

The advantages of using fluidized coke instead of the gaseous reductants are well documented by A.I. It appears that the filtered melt at approximately 850°F will be pumped to the reducer which should operate at about 1500°F in order to get a rapid rate of reduction of all sulfur to the sulfide form in about 15 minutes. Heat of reaction must be supplied as well as heat required to go from 850 to 1500°F. Excess carbon must be present and sufficient oxygen for the heat generating reaction to maintain temperature.

AI has run tests which indicate that out of a large number of possible reactions, only three overall reactions predominate, namely, $4\ M_2SO_3 \longrightarrow 3\ M_2SO_4 + M_2S$ (1)

$M_2S + 2\ O_2 \longrightarrow M_2SO_4$ + heat (major) (2)

$M_2SO_4 + 2\ C \longrightarrow M_2S + CO_2$ - heat (3)

Therefore, it is necessary to continually supply coke and melt with sufficient oxygen to maintain the melt temperature at about 1500°F.

It appears that the disproportionation reaction (1) will be very rapid and so will the oxidation of sulfide to sulfate, reaction (2), which liberates about 230 Kcal per mole Na_2S (1340°F). Heat liberated from reaction (1) is very minor. Thus heating up of the melt appears to be no problem. However, carbon must be present to reduce the sulfate to sulfide which will consume about 43 Kcal/mole Na_2S (1340°F). Although this last reaction may not be as rapid as the others, it is still a fast reaction if good contact and sufficient coke (excess) is available.

Since all the reactions are very rapid, the major concern should be with the mechanical end of getting good mixing in order to take advantage of these rapid reactions. If the melt is quiescent, most of the coke will rise to the surface; only when a gas, i.e., air and/or recycle gas, is bubbled through the melt may sufficient agitation be available for good mixing. Recycle gas is mentioned because the air must be controlled to amounts which may be less than sufficient for good mixing, above 0.25 ft/sec superficial gas velocity. As the fluid coke is consumed, the remaining particles will tend to flow with the melt as well as some of the initial fine particles, thus a coke separation problem exists and should be studied. A settling zone (upward for coke) may be a solution.

Another point of importance is the concentration of carbon dioxide in the off-gas from the reducer. If air and/or recycled gas are used in the reducer, will the carbon dioxide content in the off-gas be enough to use in the regenerator? Perhaps a particular design for the reducer can yield the proper CO_2 content stream.

A.I. have considered the effect of bed expansion and did show advantageously that coke in the melt at the level of 6.25% did significantly lower bed expansion. One questions the superficial gas velocities on the figure reporting this work, it was presumed that 20 was 0.2 and 40 was 0.4 ft/sec. More investigation of bed expansion, foaming or frothing, and salt entrainment should be done with melts simulating reducer conditions. This will be important for design.

The CO_2/CO ratio of the off gas from the reducer has been looked at and reported to be about 5-6/1. One must be cautious in analyzing gases of this type coming out of a reactor at high temperature because of possible gas phase reactions occurring after leaving the hot melt. Normal techniques use probes which take samples directly above the melt and attempt to freeze the gas composition by sudden cooling. If all the oxygen gets consumed in the melt a probe is unnecessary, but if oxygen exits then any CO can be oxidized to CO_2 at these temperatures and the results do not reflect the true conditions. After-burning may be necessary to convert any CO to CO_2 before using this gas in the regenerator. Possibility of COS formation exists.

Since the rates of reaction are quite fast and materials handling is probably more of a problem, then it hardly seems necessary that catalysis by added iron, except for that which is present in the melt, need be considered at this time. It may also cause frothing and require separation before the melt can be regenerated.

Specifications on coke may be required. Volatile matter can vary widely and AI has shown that calcined (temperature unknown) delayed coke was poor. Since the reducer operates at about 1500°F any coke could be preheated to about this temperature to lower volatile matter and not change the reactivity of the carbon appreciably.

5. Regenerator

The regeneration reaction is,

$$M_2S(l) + CO_2(g) + H_2O(g) \rightleftharpoons M_2CO_3(l) + H_2S(g) + \text{heat.}$$

From literature data on sodium sulfide and potassium sulfide, the reaction as written is favored at low temperatures and the reverse reaction is favored at high temperatures. This was substantiated by experimental data at 800°, 930° and 1110°F. Choice of about 900°F for regeneration appears to give rapid equilibrium and a suitable equilibrium constant of about 10. Equilibrium runs made by Atomics International established that the reaction is exothermic, ΔH is -23 Kcal/mole M_2S in the range 850-1125°F using mole fractions instead of activities for the liquids and ignoring side reactions. Estimate of the effect of the side reaction, $CO_2 + M_2S = M_2CO_2S$, monothiocarbonate formation, indicated that ΔH could be -28 as an upper limit. Non ideal liquid behavior, i.e. effect of activities, would tend to lower the ΔH value. Therefore the result appears satisfactory.

Considerable chemistry is involved in passing CO_2 into the $M_2S \cdot M_2CO_3$ melt. AI have performed a number of experiments to try to unravel this system. The results of these experiments and the negative effect of increasing CO_2 pressure on H_2S removal indicated that thiocarbonate formation appears to be the best plausible answer. No direct analysis for thiocarbonate was made however. The effective K_e for regeneration which incorporates the pressure effect of carbon dioxide appears to give reasonable agreement between calculated and experimental values,

$$K_e = \frac{1.90 \times 10^{-6} \exp (28{,}000/RT)}{[1 + P_{CO_2} \times 1.24 \times 10^{-3} \exp (\frac{15{,}400}{RT})]} .$$

Therefore less than 0.5 atm of CO_2 in regenerator gases is recommended by AI to keep thiocarbonate formation minimal.

Investigation of the ratio of CO_2 to H_2O in the gas to the regenerator indicated 1 to 1 gave maximum conversion providing the melt did not absorb large amounts of CO_2.

The desired concentration of sulfide in and out of the regenerator was not established. However, it was shown that when the mole fraction of M_2S reached less than 0.02 mole % (1.4 wt.%), there was a rapid drop in H_2S content in the effluent gas. If the absorber can tolerate 1.4 wt.% M_2S without loss of sulfur as H_2S into the flue gas, then this looks like a satisfactory working melt.

Analysis of the rate of reaction data by AI indicated equilibrium was attained very rapidly and that there was a dependence on the incoming gas rate. It appeared that when gas rates were pushed up to what would be considered for engineering design, the equipment plugged up due to salt entrainment, etc. Better designed experimental equipment is needed which will allow proper gas flows. Design must consider melt entrainment in the off-gases.

A disadvantage of having iron present in the melt while regenerating was the enhanced foaming and insoluble potassium iron III sulfide, $KFeS_2$, formation. Thus, it does appear that added iron or other catalysts should be avoided in the melt to the regenerator.

Regeneration time of 20 - 30 minutes appears feasible with properly designed equipment and with good gas-liquid contact. The 1500°F melt out of the reducer will have to be cooled down to 850-900°F for the regenerator and heat will have to be removed from the regenerator due to the exothermic reaction.

6. Miscellaneous

From the very complete corrosion investigation of metals only 347 stainless steel appears satisfactory at temperatures below 950°F, therefore this may be the metal for the absorber, pumps, filter, piping and possibly the regenerator. For the reducer and melt piping which operates at about 1500°F, AI suggests Haynes LT-1 (cermet), α-Al_2O_3, or a cooled steel surface with frozen melt on the surface to protect it. Additional testing and evaluation of these high temperature materials at process conditions appears desirable.

The chemistry of the lithium recovery appears satisfactory. One wonders whether potassium and sodium recovery should also be practiced since consideration must be given to possible pollution from discarded streams.

C. MECHANICAL

1. Coke Handling

This process uses green delayed high-sulfur petroleum coke as a reducing agent. Although 2" coke might be used for reduction, a crushing and screening circuit has been included to reduce the coke size from 2" to minus 1/4". If the need for crushing is uncertain, this indicates that the reducing equipment might easily accept a nominal amount of oversize. If so, the crushing and screening circuit could be simplified by eliminating the closed circuit screen entirely and making a single pass through the crusher. This would not only remove the cost and operation of a piece of equipment, but it would eliminate the circulating load on the bucket elevator and crusher, reducing their size and cost.

The crusher choice for this service is unusual. It is a two-rotor cage mill and it will produce a product with a large percentage of fines. If the process doesn't require this, a simple impactor could be sutstituted to save cost and power.

A few errors and ommissions were noted in the estimate of the coke handling equipment.

a. The bucket elevator which feeds the coke crusher was not rated to include the circulating load.

b. A belt conveyor is required to convey the crushed, sized coke from the screen to the coke silo feed elevator. This conveyor is shown on the arrangement drawings but is omitted from the flow sheet and cost tabulation.

c. Two feeders should be provided at the coke silos to feed the elevating belt conveyor.

d. Dust collecting equipment should be added to provide pick-up points at the following locations:

1) The feed chute to the reversing conveyor over the coke silos.

2) The feed chutes from the coke silos to the elevating belt conveyor.

3) The tranfer chute from the elevating conveyor to the tripper belt over the coke bins.

4) The four coke bins.

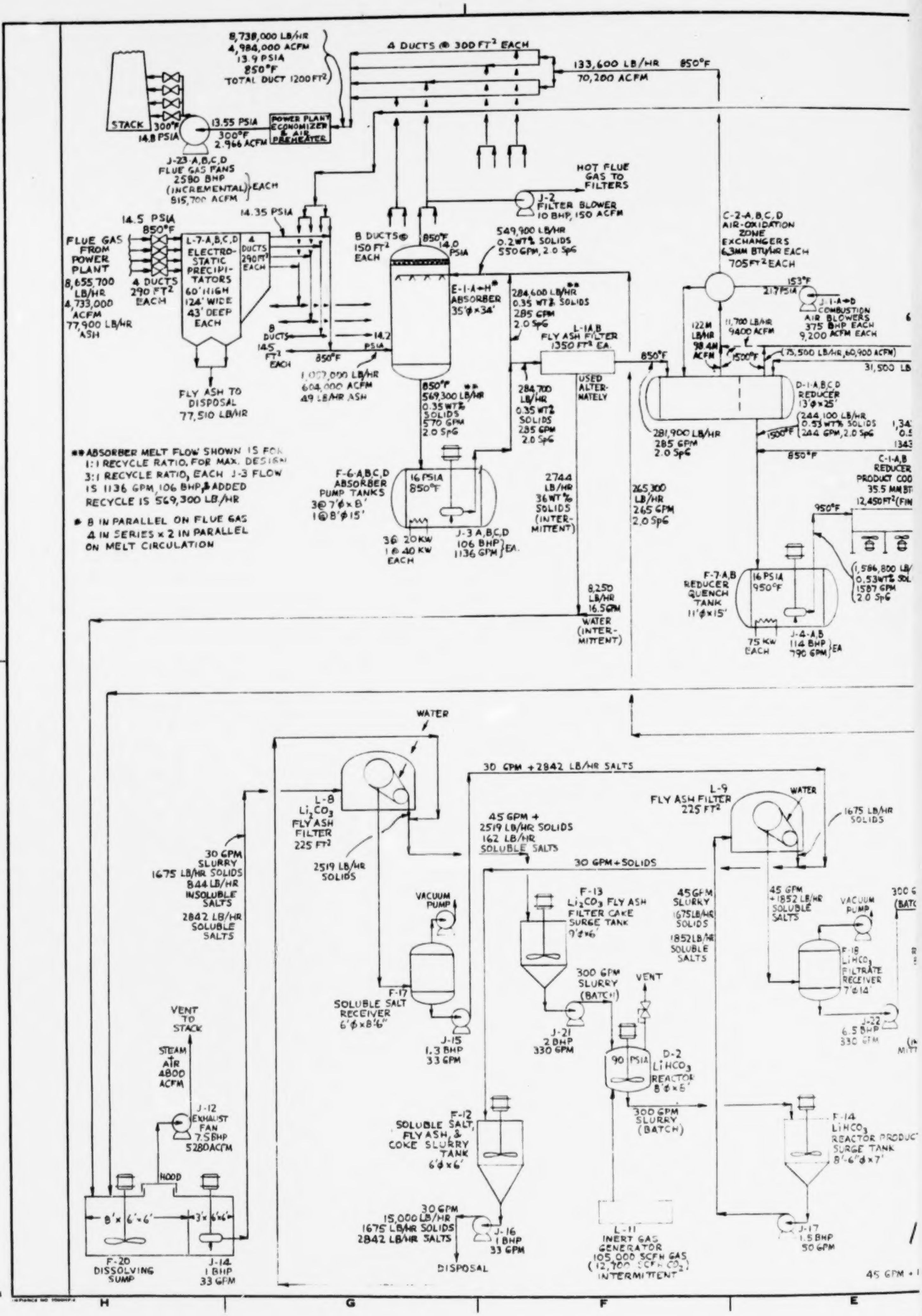
2. $Li_2 CO_3$ Recovery Area

The flow diagram and equipment cost estimate have omitted a feeder under the surge drum between the filter and dryer. The drum should be equipped with a type of feeder which will insure positive discharge from the drum and a steady, controllable feed to the dryer.

3. M_2CO_3 Make-up Area

The carbonate bucket elevator has not been provided with a truck hopper, or feeder. A truck dump hopper with capacity for one and a half to two truckloads should be added to the estimate.

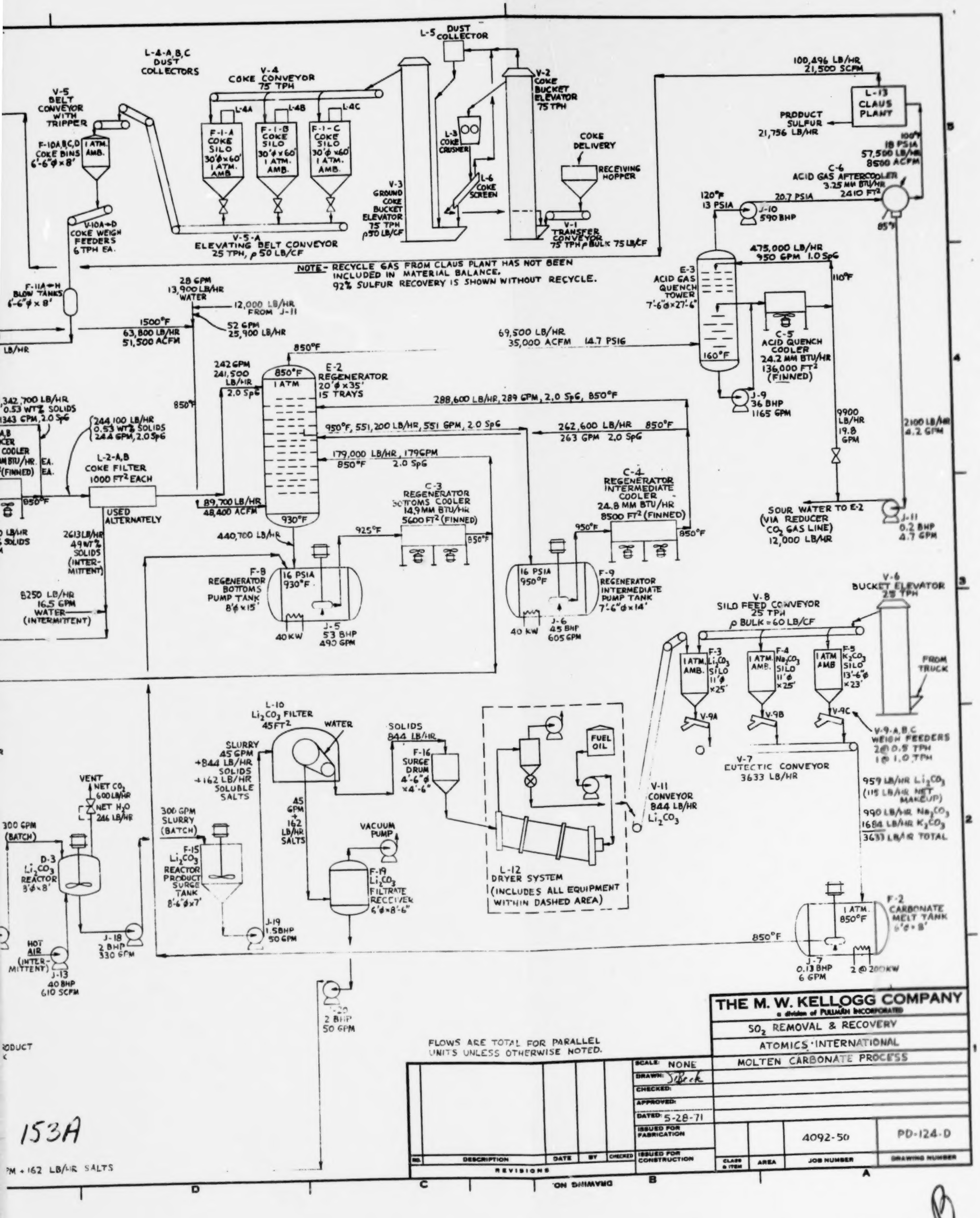
A dust collecting connection should be provided at the loading point for the silo feed conveyor.


8,738,000 LB/HR
4,984,000 ACFM
13.9 PSIA
850°F
TOTAL DUCT 1200 FT²
4 DUCTS @ 300 FT² EACH
133,600 LB/HR 850°F
70,200 ACFM
STACK
300°F
14.8 PSIA
13.55 PSIA
300°F
2,966 ACFM
POWER PLANT ECONOMIZER & AIR PREHEATER
J-23-A,B,C,D
FLUE GAS FANS
2580 BHP
(INCREMENTAL) EACH
815,700 ACFM
HOT FLUE GAS TO FILTERS
J-2
FILTER BLOWER
10 BHP, 150 ACFM
14.5 PSIA
850°F
FLUE GAS FROM POWER PLANT
8,655,700 LB/HR
4,733,000 ACFM
77,900 LB/HR ASH
4 DUCTS 290 FT² EACH
L-7-A,B,C,D
ELECTROSTATIC PRECIPITATORS
60' HIGH
124' WIDE
43' DEEP
EACH
4 DUCTS 290 FT² EACH
14.35 PSIA
8 DUCTS @ 150 FT² EACH
850°F
14.0 PSIA
549,900 LB/HR
0.2 WT% SOLIDS
550 GPM, 2.0 SpG
E-1-A→H*
ABSORBER
35'ϕ×34'
284,600 LB/HR**
0.35 WT% SOLIDS
285 GPM
2.0 SpG
L-1A,B
FLY ASH FILTER
1350 FT² EA.
8 DUCTS
145 FT² EACH
14.2 PSIA
850°F
1,007,000 LB/HR
604,000 ACFM
49 LB/HR ASH
FLY ASH TO DISPOSAL
77,510 LB/HR
850°F **
569,300 LB/HR
0.35 WT% SOLIDS
570 GPM
2.0 SpG
284,700 LB/HR
0.35 WT% SOLIDS
285 GPM
2.0 SpG
USED ALTERNATELY
F-6-A,B,C,D
ABSORBER PUMP TANKS
3@7'ϕ×8'
1@8'ϕ15'
16 PSIA
850°F
36 20 KW
1 @ 40 KW
EACH
J-3 A,B,C,D
106 BHP
1136 GPM EA.
2744 LB/HR
36 WT %
SOLIDS
(INTERMITTENT)
8,250 LB/HR
16.5 GPM
WATER (INTERMITTENT)
265,300 LB/HR
265 GPM
2.0 SpG
C-2-A,B,C,D
AIR-OXIDATION ZONE EXCHANGERS
6.3MM BTU/HR EACH
705 FT² EACH
153°F
21.7 PSIA
J-1-A→D
COMBUSTION AIR BLOWERS
375 BHP EACH
9,200 ACFM EACH
122 M LB/HR
98.4 M ACFM
11,700 LB/HR
9400 ACFM
1500°F
(75,500 LB/HR, 60,900 ACFM)
31,500 LB
850°F
D-1-A,B,C,D
REDUCER
13'ϕ×25'
244,100 LB/HR
0.53 WT% SOLIDS
244 GPM, 2.0 SpG
1500°F
281,900 LB/HR
285 GPM
2.0 SpG
850°F
1,34
0.5
1343
C-1-A,B
REDUCER
PRODUCT COO
35.5 MM BT
12,450 FT² (FIN
950°F
F-7-A,B
REDUCER QUENCH TANK
11'ϕ×15'
16 PSIA
950°F
75 KW EACH
J-4-A,B
114 BHP
790 GPM EA
1,586,800 LB/
0.53 WT% SOL
1587 GPM
2.0 SpG
6
WATER
L-8
Li₂CO₃
FLY ASH FILTER
225 FT²
2519 LB/HR SOLIDS
30 GPM + 2842 LB/HR SALTS
45 GPM +
2519 LB/HR SOLIDS
162 LB/HR
SOLUBLE SALTS
30 GPM
SLURRY
1675 LB/HR SOLIDS
844 LB/HR INSOLUBLE SALTS
2842 LB/HR SOLUBLE SALTS
VACUUM PUMP
F-17
SOLUBLE SALT RECEIVER
6'ϕ×8'6"
J-15
1.3 BHP
33 GPM
30 GPM + SOLIDS
F-13
Li₂CO₃ FLY ASH FILTER CAKE SURGE TANK
9'ϕ×6'
300 GPM
SLURRY
(BATCH)
J-21
2 BHP
330 GPM
VENT
90 PSIA
D-2
LiHCO₃
REACTOR
8'ϕ×6'
300 GPM
SLURRY
(BATCH)
L-9
FLY ASH FILTER
225 FT²
WATER
1675 LB/HR SOLIDS
45 GPM
SLURRY
1675 LB/HR SOLIDS
1852 LB/HR SOLUBLE SALTS
45 GPM
+ 1852 LB/HR
SOLUBLE SALTS
VACUUM PUMP
F-18
LiHCO₃
FILTRATE RECEIVER
7'ϕ14'
J-22
6.5 BHP
330 GPM
300 G
(BATC
VENT TO STACK
STEAM + AIR
4800 ACFM
J-12
EXHAUST FAN
7.5 BHP
5280 ACFM
HOOD
8'×6'×6'
3'×6'×6'
F-20
DISSOLVING SUMP
J-14
1 BHP
33 GPM
F-12
SOLUBLE SALT, FLY ASH, & COKE SLURRY TANK
6'ϕ×6'
30 GPM
15,000 LB/HR
1675 LB/HR SOLIDS
2842 LB/HR SALTS
J-16
1 BHP
33 GPM
DISPOSAL
L-11
INERT GAS GENERATOR
105,000 SCFH GAS
(12,700 SCFH CO₂)
INTERMITTENT
F-14
LiHCO₃
REACTOR PRODUC
SURGE TANK
8'-6"ϕ×7'
J-17
1.5 BHP
50 GPM
45 GPM +
H
G
F
E
34

** ABSORBER MELT FLOW SHOWN IS FOR 1:1 RECYCLE RATIO. FOR MAX. DESIGN 3:1 RECYCLE RATIO, EACH J-3 FLOW IS 1136 GPM, 106 BHP, & ADDED RECYCLE IS 569,300 LB./HR

* 8 IN PARALLEL ON FLUE GAS
4 IN SERIES × 2 IN PARALLEL ON MELT CIRCULATION

A


L-4-A,B,C DUST COLLECTORS
V-4 COKE CONVEYOR 75 TPH
L-5 DUST COLLECTOR
V-2 COKE BUCKET ELEVATOR 75 TPH
V-5 BELT CONVEYOR WITH TRIPPER
F-10A,B,C,D COKE BINS 6'-6"ϕ × 8'
1 ATM. AMB.
L-4A
L-4B
L-4C
F-1-A COKE SILO 30'ϕ × 60' 1 ATM. AMB.
F-1-B COKE SILO 30'ϕ × 60' 1 ATM. AMB.
F-1-C COKE SILO 30'ϕ × 60' 1 ATM. AMB.
L-3 COKE CRUSHER
L-6 COKE SCREEN
V-3 GROUND COKE BUCKET ELEVATOR 75 TPH ρ50 LB/CF
COKE DELIVERY
RECEIVING HOPPER
V-1 TRANSFER CONVEYOR 75 TPH ρ BULK 75 LB/CF
V-10A→D COKE WEIGH FEEDERS 6 TPH EA.
V-5-A ELEVATING BELT CONVEYOR 25 TPH, ρ 50 LB/CF
100,496 LB/HR 21,500 SCFM
L-13 CLAUS PLANT
PRODUCT SULFUR 21,756 LB/HR
100°F 18 PSIA 57,500 LB/HR 8500 ACFM
C-6 ACID GAS AFTERCOOLER 3.25 MM BTU/HR 2410 FT²
120°F 13 PSIA
20.7 PSIA
J-10 590 BHP
85°F
NOTE- RECYCLE GAS FROM CLAUS PLANT HAS NOT BEEN INCLUDED IN MATERIAL BALANCE. 92% SULFUR RECOVERY IS SHOWN WITHOUT RECYCLE.
F-11A→H BLOW TANKS 6'-6"ϕ × 8'
28 GPM 13,900 LB/HR WATER
12,000 LB/HR FROM J-11
1500°F 63,800 LB/HR 51,500 ACFM
52 GPM 25,900 LB/HR
LB/HR
E-3 ACID GAS QUENCH TOWER 7'-6"ϕ×27'-6"
475,000 LB/HR 950 GPM 1.0 SpG
110°F
69,500 LB/HR 35,000 ACFM 14.7 PSIG
160°F
C-5 ACID QUENCH COOLER 24.2 MM BTU/HR 136,000 FT² (FINNED)
J-9 36 BHP 1165 GPM
850°F
242 GPM 241,500 LB/HR 2.0 SpG
850°F 1 ATM
E-2 REGENERATOR 20'ϕ × 35' 15 TRAYS
850°F
288,600 LB/HR, 289 GPM, 2.0 SpG, 850°F
,342,700 LB/HR 0.53 WT% SOLIDS 1343 GPM, 2.0 SpG
244,100 LB/HR 0.53 WT% SOLIDS 244 GPM, 2.0 SpG
950°F, 551,200 LB/HR, 551 GPM, 2.0 SpG
262,600 LB/HR 850°F 263 GPM 2.0 SpG
9900 LB/HR 19.8 GPM
2100 LB/HR 4.2 GPM
COOLER
MM BTU/HR. EA.
(FINNED) EA.
L-2-A,B COKE FILTER 1000 FT² EACH
179,000 LB/HR, 179 GPM 850°F 2.0 SpG
C-4 REGENERATOR INTERMEDIATE COOLER 24.8 MM BTU/HR 8500 FT² (FINNED)
850°F
USED ALTERNATELY
89,700 LB/HR 48,400 ACFM
930°F
C-3 REGENERATOR BOTTOMS COOLER 14.9 MM BTU/HR 5600 FT² (FINNED)
SOUR WATER TO E-2 (VIA REDUCER CO₂ GAS LINE) 12,000 LB/HR
J-11 0.2 BHP 4.7 GPM
LB/HR SOLIDS
2613 LB/HR 49 WT% SOLIDS (INTERMITTENT)
440,700 LB/HR
925°F
850°F
950°F
850°F
F-8 REGENERATOR BOTTOMS PUMP TANK 8'ϕ × 15'
16 PSIA 930°F
16 PSIA 950°F
F-9 REGENERATOR INTERMEDIATE PUMP TANK 7'-6"ϕ × 14'
V-6 BUCKET ELEVATOR 25 TPH
8250 LB/HR 16.5 GPM WATER (INTERMITTENT)
40 KW
J-5 53 BHP 490 GPM
40 KW
J-6 45 BHP 605 GPM
V-8 SILO FEED CONVEYOR 25 TPH ρ BULK = 60 LB/CF
1 ATM. AMB.
F-3 Li₂CO₃ SILO 11'ϕ × 25'
F-4 Na₂CO₃ SILO 11'ϕ × 25'
F-5 K₂CO₃ SILO 13'-6"ϕ × 23'
FROM TRUCK
V-9A
V-9B
V-9C
V-9-A,B,C WEIGH FEEDERS 2@0.5 TPH 1@1.0 TPH
L-10 Li₂CO₃ FILTER 45 FT²
WATER
SOLIDS 844 LB/HR
F-16 SURGE DRUM 4'-6"ϕ × 4'-6"
FUEL OIL
V-7 EUTECTIC CONVEYOR 3633 LB/HR
SLURRY 45 GPM +844 LB/HR SOLIDS +162 LB/HR SOLUBLE SALTS
VENT
NET CO₂ 600 LB/HR
NET H₂O 246 LB/HR
45 GPM + 162 LB/HR SALTS
V-11 CONVEYOR 844 LB/HR Li₂CO₃
959 LB/HR Li₂CO₃ (115 LB/HR NET MAKEUP)
990 LB/HR Na₂CO₃
1684 LB/HR K₂CO₃
3633 LB/HR TOTAL
300 GPM (BATCH)
300 GPM SLURRY (BATCH)
VACUUM PUMP
D-3 Li₂CO₃ REACTOR 8'ϕ × 8'
F-15 Li₂CO₃ REACTOR PRODUCT SURGE TANK 8'-6"ϕ × 7'
F-19 Li₂CO₃ FILTRATE RECEIVER 6'ϕ × 8'-6"
L-12 DRYER SYSTEM (INCLUDES ALL EQUIPMENT WITHIN DASHED AREA)
F-2 CARBONATE MELT TANK 6'ϕ × 8'
1 ATM. 850°F
850°F
HOT AIR (INTERMITTENT)
J-13 40 BHP 610 SCFM
J-18 2 BHP 330 GPM
J-19 1.5 BHP 50 GPM
J-7 0.13 BHP 6 GPM
2 @ 200 KW
J-20 2 BHP 50 GPM
RODUCT

FLOWS ARE TOTAL FOR PARALLEL UNITS UNLESS OTHERWISE NOTED.

153A

PM + 162 LB/HR SALTS

THE M. W. KELLOGG COMPANY
a division of PULLMAN INCORPORATED

SO$_2$ REMOVAL & RECOVERY
ATOMICS INTERNATIONAL
MOLTEN CARBONATE PROCESS

NO.	DESCRIPTION	DATE	BY	CHECKED
REVISIONS				

SCALE: NONE
DRAWN: JBeck
CHECKED:
APPROVED:
DATED: 5-28-71
ISSUED FOR FABRICATION
ISSUED FOR CONSTRUCTION

CLASS & ITEM	AREA	JOB NUMBER	DRAWING NUMBER
		4092-50	PD-124-D

D C B A

5 4 3 2 1

DRAWING NO.

POTASSIUM FORMATE PROCESS FOR REMOVING SO_2 FROM STACK GAS

A. PROCESS

1. Process Description (See MWK Dwg No. PD-111-D)

In this process, stack gas is scrubbed at 200°F with an excess of 85% aqueous solution of potassium formate to form potassium thiosulfate. The solution is then heated to 540°F at 520 psig and the excess formate reduces the thiosulfate to potassium hydrosulfide. The hydrosulfide is then stripped with carbon dioxide and steam thereby producing hydrogen sulfide from which elemental sulfur is recovered in a three-stage Claus plant. The stripped solution is predominantly a mixture of potassium bicarbonate and carbonate. This mixture is regenerated to potassium formate by reaction with carbon monoxide at a total pressure of 2000 psig and a temperature of 540°F. The formate solution is then recycled to the stack gas scrubber.

The main chemical reactions involved in the potassium formate process are summarized below in the same sequence they occur in the process.

Scrubbing Reaction

$$2\ KOOCH + 2\ SO_2 = K_2S_2O_3 + 2\ CO_2 + H_2O$$

Reduction Reactions

$$4\ KOOCH + K_2S_2O_3 = 2\ K_2CO_3 + 2\ KHS + 2\ CO_2 + H_2O$$

$$K_2CO_3 + CO_2 + H_2O = 2\ KHCO_3$$

Stripping Reactions

$$2\ KHS + CO_2 + H_2O = K_2CO_3 + 2\ H_2S$$

$$KHCO_3 + KHS = K_2CO_3 + H_2S$$

Regeneration Reaction

$$K_2CO_3 + 2\ CO + H_2O = 2\ KOOCH + CO_2$$

The overall reaction of the formate process may be written as:

$$SO_2 + 3\ CO + H_2O = H_2S + 3\ CO_2$$

2. Process Design Basis

This process has been evaluated for operation with a new 1000 MW power plant. The design criteria used in evaluation of the formate process are given below:

Plant Size	1000 MW
Heat Rate	9000 Btu/kwhr
SO_2 Removal	90%
Excess Air	20%
Carbon Burned in Coal	100%
Heating Value in Coal	
Wet	11,980 Btu/lb
Dry	12,580 Btu/lb
Sulfur to SO_2	98%
Sulfur to SO_3	2%
Ash in Coal to Fly Ash	71.7%
Temperature out of Air Preheater (nominal)	300°F
Minimum Gas Temperature to Stack After Treatment	200°F
Preferable Gas Temperature to Stack After Treatment	250°F or higher
Gas Velocities in Ducts	60 ft/sec
Flue Gas Quantity	293,000 moles/hr
Flue Gas Molecular Weight	29.54
Fly Ash	77900 lbs/hr

Flue Gas Composition

Component	Mole Fraction
SO_2	0.00261
SO_3	0.00005
CO_2	0.13657
N_2	0.74087
O_2	0.03276
H_2O	0.08714

Coal Composition

Component	Dry Wt. %
Ash	15.2
S	3.5
H_2	5.0
C	67.2
N	1.6
O	7.5
Water in Coal	4.8 lbs/100 lbs wet

Design criteria related specifically to the potassium formate process are discussed in the section Process Design Rationale.

3. Process Design Rationale

The lack of information and data on this process made it necessary to make many assumptions before a process flow sheet could be defined and evaluated. The subsequent discussion will give the assumptions made and design criteria used in evaluating this process.

Stack gas flows through cyclone separators where 80% of the fly ash is removed. It is assumed that since the Formate process is a wet scrubbing process, the fly ash remaining in the flue gas effluent from the cyclones will be removed in the stack gas scrubbers.

Flue gas flows from the cyclones into the stack gas scrubbers. From the article describing the Formate process, there does not appear to be any appreciable back pressure of SO_2 in the aqueous formate solution. The absorbers were therefore sized assuming no SO_2 back pressure. A three stage spray column would give 90% removal of SO_2 from the stack gas assuming tower efficiency to be 60%. A linear gas velocity of 500 ft/min was used to determine the tower area. Based on the limited amount of available data, it appears that a liquid recirculation rate lower than that used in the laboratory would be adequate. For this evaluation a liquid rate of 230 lbs/hr ft^2 was used but it should be noted that if rates 5-fold higher were used, the effect on the overall plant economics would be slight. The tower operates at 200°F with an 85% solution of potassium formate. The experimental work done at these conditions indicates that water is not evaporated and the scrubber stays in water balance. Since enthalpy data were not available on the absorption system it was assumed that the absorbers are in heat balance. It was further assumed that the SO_3 in the stack gas is converted to K_2SO_4 and the sulfate precipitates out of solution but all other potassium salts would stay in solution. The formate solution was assumed to remove the fly ash remaining in the stack gas downstream of the cyclones and the fly ash could be slurried in the formate solution.

It was assumed that centrifuges could handle the formate-fly ash slurry effluent from the scrubber to separate out the fly ash. If filters were used instead of centrifuges an electrostatic precipitator would be required instead of cyclones since filters can handle a solution with only about 0.1% fly ash; thus fly ash removed in the precipitators would have to be 99.5%. The solids stream discharged by the centrifuge is assumed to contain 20 weight percent liquid. To keep potassium losses low, three centrifuges in series are used with a water wash (reslurry) between each centrifuge.

The ash free solution is sent to the reducing reactor which is designed as a continuous stirred tank with a 20 minute holding time. This is the same holdup as that reported in the ACS paper. Temperature and pressure are also the same as that demonstrated in the laboratory (540°F, 520 psig). In the reactor all the potassium thiosulfate is assumed to be converted to the hydrosulfide. While passing through the centrifuges, the solution was diluted from 85% to 58% potassium salts but it is assumed that this dilution does not affect the reaction rate in the reducer.

The reduced potassium salts from the reducing reactor are sent to the E-2 stripper. The concentration of H_2S in this stripper off-gas was assumed to be 25% based on the batch stripping data presented in the ACS report where about 30% H_2S was initially observed. Stripping is done with CO_2 and steam. Enthalpy data are again lacking and a heat balance could not be made on this tower.

The H_2S-rich gas is sent to a Claus reactor where elemental sulfur is recovered. Recovery of the available sulfur in the Claus plant is 97.5%; oxygen rather than air is used in this plant for the combustion of the H_2S. Since carbon dioxide leaving the Claus plant is recovered but must be compressed before absorption, use of air instead of oxygen would greatly increase the compressor size due to the nitrogen in the air.

Gases leaving the Claus plant are rich in carbon dioxide. As suggested by the ACS paper, a hot potassium carbonate absorption-desorption system is used to recover 98% of the available CO_2. Since additional CO_2 is required to keep the plant in carbon balance (CO_2 is lost in the stack gas scrubber), makeup CO_2 from the reformer is used. Sulfur dioxide leaving the Claus plant is assumed to be absorbed by the K_2CO_3 to give potassium sulfite.

This K_2SO_3 represents an expensive potassium loss but potassium values probably could be recovered by additional processing in equipment (L-5) which has yet to be defined.

In the formate regenerator (D-2), experimentally it required two hours to convert the carbonate to formate. The reason for the long residence time was attributed to the experimental equipment. It was assumed with proper agitation only a 25 minute residence time would be needed. Experimentally pure CO was used with an inlet partial pressure of 700 psi and the water vapor pressure of the 60% carbonate solution at reaction conditions was 500 psi. A commercial reformer will produce only about 50% CO maximum. Consequently, the commercial reactor must operate at 2000 psig to keep the inlet partial pressure of CO at 700 psi. Thermodynamic data were not available for this reaction. Estimates of the heat of reaction were made based on using sodium formate and the reaction was found to be exothermic. It was assumed that the excess water would be evaporated from the reactor to bring the exit product formate concentration to the desired 85% level. The regenerator exit gas, which is rich in CO_2 and CO, is recycled to the reformer.

Natural gas reforming of CO_2 is used to generate the CO needed for the regenerator. The main reaction in the reformer was assumed to be

$$CH_4 + CO_2 = 2\,CO + 2H_2$$

The heat required for the endothermic reaction is provided by combustion of natural gas with air. Part of the combustion gas is used to supply the makeup CO_2 needed in the plant.

4. Process Appraisal

The basic concept of the potassium formate process is defined in the ACS paper. The experimentation done on this process demonstrates only the basic concept and this limited data can be used only for a very preliminary process design and economic evaluation. Additional data are required in every facet of this process. Before discussing those areas which need further clarification, the advantages and disadvantages of this process will be given.

Advantages

- Wet scrubbing of flue gas at 200°F eliminates the need for reheat to get plume rise.
- The apparent efficiency of absorption indicates that the SO_2 absorbed has no back pressure in the formate solution. This great affinity keeps the liquid recirculation rate down to relatively low levels and provides nearly complete removal of SO_2.
- The use of liquid scrubbing may make the use of electrostatic precipitators unnecessary if centrifuges can be designed to handle the fly ash slurry formed with the potassium formate solution.
- The SO_2 is recovered as elemental sulfur rather than H_2SO_4 thur providing greater flexibility in handling, storage, and marketing.

Disadvantages

- Being a liquid scrubbing process, some spray will pass through even the most efficient demisters. Potassium salts are expensive and losses represent large operating expense. It would also be undesirable to have appreciable quantities of formate or carbonate contained in the exit flue gases since there could be as bad or worse pollutants than the sulfur oxides.
- The operating pressure of the formate regenerator is high (2000 psig) because the reducing gas in a commercial unit contains a maximum of 50% CO. The slow reaction rate and high pressure of regeneration impose severe design problems on the reactor.
- The need for recovering the CO_2 after the Claus plant may pose problems in the hot potassium carbonate recovery system as suggested in the ACS paper. Any unconverted sulfur leaving the Claus system as SO_2 will be absorbed and reacted with the K_2CO_3. This represents intolerably high potassium loses and consequently requires additional processing which has yet to be defined.
- As in the stack gas scrubber, the hot carbonate recovery system is a source of potassium loss due to mist formation.

The data required to give a complete definition of the process for detailed design must be obtained experimentally. Literature sources are expected to give only a minimal amount of information pertinent to this process. Experimental data required are processing and thermodynamic. The thermodynamic data requirements are as follows:

- Vapor pressure of water over the potassium salt solutions.
- Solubility data of the different potassium salts in water and each other, i.e. phase diagrams.
- Heat of reaction data – probably available in the literature.
- Heat of mixing and solution data.

The different chemical processing steps of the formate process must each be experimentally studied. Those areas where processing studies are required are discussed below:

- Scrubbing
  Experimental tests must be made to obtain data on the effect of the variables such as temperature (concentration), liquid to gas rate and conversion levels of potassium formate on mass transfer rate. The effect of nitrogen oxides on the absorption must also be determined. The rheological properties of the resultant fly ash slurries produced with the aqueous potassium solutions should also be determined and proposed methods of separating the fly ash should be confirmed.

- Reduction
  This reaction must be studied to determine the effects of temperature, pressure, residence time, fly ash content, water concentrations and stability of the potassium

formate. The results given in the ACS paper shows potassium sulfate being formed and eliminated. Side reactions producing K_2SO_4 are a source of potassium loss.

- Stripping
  Variables affecting the stripping of the sulfur values in the reduced potassium salt solution are CO_2/steam ratio, temperature, pressure and solution concentration. This reaction step does not seem to present any major problems.

- Regeneration
  This reaction step appears to be the most difficult one. The variables to be studied which affect reaction rate are temperature, pressure, CO partial pressure in the reducing gas, H_2/CO ratio, concentration of the reacting solution and mechanical mixing effects on the mass transfer rate. Effects of foaming and expansion may pose serious problems (increased reactor size) and must be determined.

In addition to the above basic area of study required in the formate process, some of the associated facilities used in this process also must be examined.

- Recovery of CO_2 in Hot Potassium Carbonate
  The use of potassium carbonate absorption of carbon dioxide may be undesirable owing to the losses of potassium incurred by reaction with sulfur dioxide leaving the Claus plant. Other absorption systems should be evaluated for applicability to the formate process. If hot potassium carbonate sorption is used then the additional processing to recover the potassium values from the sulfite formed must be defined.

- Reforming
  It was proposed in the ACS paper that natural gas reforming with CO_2 be used to produce the required reducing gas. Although this reaction is known it has not been used on a commercial scale and may require additional experimentation.

In addition to the studies made on the individual steps of this process an integrated pilot plant must be operated to demonstrate to total system. This is required because recycle streams may build up undesirable compounds and bleed streams would have to be used to eliminate these compounds.

Source of Data

The process design and evaluation is based entirely on a paper presented at the ACS National Meeting in Houston on February 22-27, 1970(1). No other sources of data on this process were available to Kellogg for this evaluation.

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(1) Yavorsky, P. M., Mazzocco, N. J., Rutledge, G. D., and Gorin, E., *Potassium Formate Process for Removing SO_2 from Stack Gas*, Paper Presented at the ACS National Meeting in Houston, February 22-27, 1970.

B. CHEMISTRY

1. Scrubbing

The chemistry is likely to be feasible. As pointed out in the process discussion, water scrubbing upstream of the absorber eliminates the advantage of the hot scrubbing. However, eliminating the water scrubbing introduces contamination by soluble ions in the ash of the solution. This is mentioned in the previously cited ACS paper, but is not discussed in detail. No mention is made of any other ion than SO_4.

On this point the flow sheet is not worked out to a sufficient degree.

It is noted also that foaming is mentioned in a later step, where good gas-liquid contact is desired. Foaming tendencies, if they exist, are a danger to the process in that they would demand extreme care in handling. It would not be desirable or permissable to spray the countryside with mixtures of potassium thiosulfate and formate.

2. Reduction

There is uncertainty as to the water vapor pressure over the solution before and especially after reduction. It is quite likely that even with a low vapor pressure, say at 200°F and a high heat of vaporization, a relatively high water vapor pressure at 540°F will result.

In the actual experiment a reflux on the cool autoclave head can easily have hidden the evaporation by causing a sizeable reflux. This may lead to expensive changes in the flow sheet.

Table III of the ACS paper indicates feed and product analysis; from this a decrease in both potassium and sulfur content follows, which is impossible. Clarification is desirable.

Further, K_2SO_4 appears and disappears without explanation. This could possibly lead to expensive bleed stream treatments.

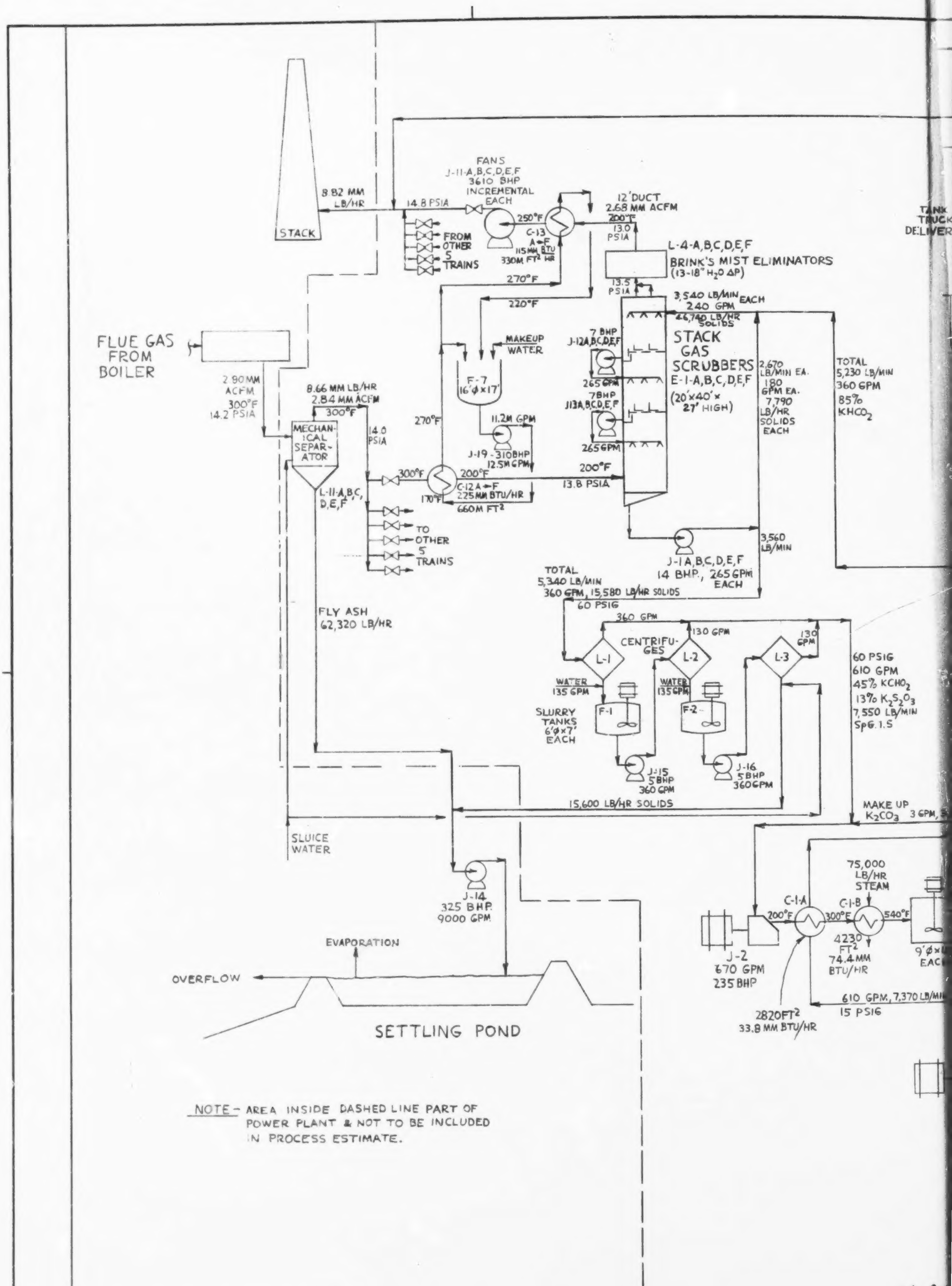
3. Stripping

Stripping has been carried out only after dilution of a typical reduced product. It is implied that one could also do this step in concentrated solution. This raises several questions.

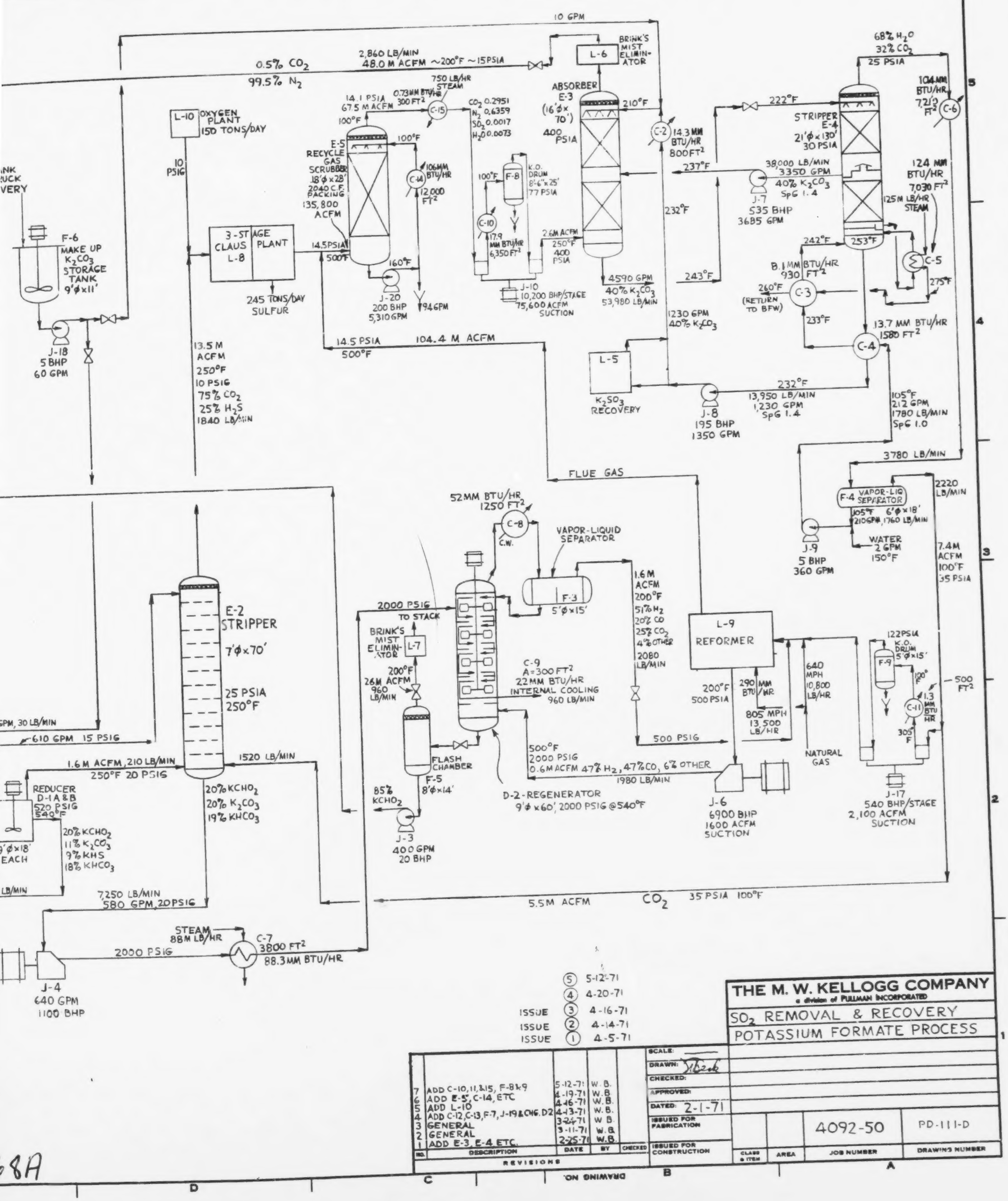
First, is it possible to have solutions before and after stripping? Second, what is the stripping factor if stripped at pressure and at temperature?

4. Conversion

Conversion seems to be limited by mass transfer, it is stated. A constant rate from zero to 80% conversion seems to bear this out. If, however, the break occurs at 80%, or in other words, if at 80% the process becomes reaction rate controlled, the overall improvement by better stirring can never be five times greater reaction rates as stated on page 21 of the ACS paper.


STACK
8.82 MM LB/HR
14.8 PSIA
FANS
J-11-A,B,C,D,E,F
3610 BHP
INCREMENTAL EACH
FROM OTHER 5 TRAINS
250°F
C-13 A→F
115MM BTU/HR
330M FT²
12' DUCT
2.68 MM ACFM
200°F
13.0 PSIA
L-4-A,B,C,D,E,F
BRINK'S MIST ELIMINATORS
(13-18" H_2O ΔP)
13.5 PSIA
270°F
220°F
3,540 LB/MIN EACH
240 GPM
46,740 LB/HR SOLIDS
TANK
TRUCK
DELIVER
FLUE GAS FROM BOILER
MAKEUP WATER
F-7
16'ϕ×17'
J-12A,B,C,D,E,F
7 BHP
STACK GAS SCRUBBERS
E-1-A,B,C,D,E,F
(20'×40'× 27' HIGH)
2,670 LB/MIN EA.
180 GPM EA.
7,790 LB/HR SOLIDS EACH
TOTAL
5,230 LB/MIN
360 GPM
85% $KHCO_2$
2.90 MM ACFM
300°F
14.2 PSIA
8.66 MM LB/HR
2.84 MM ACFM
300°F
14.0 PSIA
MECHANICAL SEPARATOR
270°F
11.2M GPM
265 GPM
7BHP
J13A,B,C,D,E,F
J-19 - 310BHP
12.5M GPM
265 GPM
300°F
200°F
200°F
13.8 PSIA
C-12A→F
225MM BTU/HR
660M FT²
170°F
L-11-A,B,C,D,E,F
TO OTHER 5 TRAINS
J-1A,B,C,D,E,F
14 BHP., 265 GPM EACH
3,560 LB/MIN
TOTAL
5,340 LB/MIN
360 GPM, 15,580 LB/HR SOLIDS
60 PSIG
FLY ASH
62,320 LB/HR
360 GPM
130 GPM
130 GPM
CENTRIFUGES
L-1
L-2
L-3
WATER 135 GPM
WATER 135 GPM
SLURRY TANKS
6'ϕ×7' EACH
F-1
F-2
J-15
5 BHP
360 GPM
J-16
5 BHP
360 GPM
60 PSIG
610 GPM
45% $KCHO_2$
13% $K_2S_2O_3$
7,550 LB/MIN
SpG. 1.5
15,600 LB/HR SOLIDS
MAKE UP
K_2CO_3
3 GPM,
SLUICE WATER
J-14
325 BHP
9000 GPM
75,000 LB/HR STEAM
C-1-A
C-1-B
200°F
300°F
540°F
J-2
670 GPM
235 BHP
4230 FT²
74.4 MM BTU/HR
9'ϕ×
EAC
610 GPM, 7,370 LB/MI
15 PSIG
2820FT²
33.8 MM BTU/HR
EVAPORATION
OVERFLOW
SETTLING POND
H
G
F
E

NOTE - AREA INSIDE DASHED LINE PART OF POWER PLANT & NOT TO BE INCLUDED IN PROCESS ESTIMATE.


10 GPM
BRINK'S MIST ELIMINATOR
L-6
0.5% CO_2
99.5% N_2
2,860 LB/MIN
48.0 M ACFM ~200°F ~15PSIA
68% H_2O
32% CO_2
25 PSIA
750 LB/HR STEAM
0.73MM BTU/HR 300 FT²
14.1 PSIA
67.5 M ACFM
100°F
C-15
CO_2 0.2951
N_2 0.6359
SO_2 0.0017
H_2O 0.0073
ABSORBER E-3 (16'ϕ x 70')
400 PSIA
210°F
C-2
14.3 MM BTU/HR 800 FT²
222°F
STRIPPER E-4 21'ϕ x 130' 30 PSIA
104 MM BTU/HR 7,210 FT²
C-6
L-10 OXYGEN PLANT 150 TONS/DAY
10 PSIG
E-5 RECYCLE GAS SCRUBBER 18'ϕ x 28' 2040 C.F. PACKING 135,800 ACFM
100°F
C-14
106MM BTU/HR 12,000 FT²
100°F
F-8
K.O. DRUM 8'-6"x 25' 77 PSIA
C-10
17.9 MM BTU/HR 6,350 FT²
237°F
38,000 LB/MIN 3350 GPM 40% K_2CO_3 SpG 1.4
J-7
535 BHP 3685 GPM
232°F
124 MM BTU/HR 7,030 FT²
125M LB/HR STEAM
F-6 MAKE UP K_2CO_3 STORAGE TANK 9'ϕ x 11'
3-STAGE CLAUS PLANT L-8
14.5PSIA 500°F
160°F
J-20 200 BHP 5,310GPM
94GPM
2.6M ACFM 250°F 400 PSIA
J-10 10,200 BHP/STAGE 75,600 ACFM SUCTION
4590 GPM 40% K_2CO_3 53,980 LB/MIN
243°F
242°F
253°F
8.1 MM BTU/HR 930 FT²
C-5
275°F
260°F (RETURN TO BFW)
C-3
233°F
245 TONS/DAY SULFUR
J-18 5 BHP 60 GPM
14.5 PSIA 500°F
104.4 M ACFM
1230 GPM 40% K_2CO_3
13.7 MM BTU/HR 1580 FT²
C-4
13.5M ACFM 250°F 10 PSIG 75% CO_2 25% H_2S 1840 LB/MIN
L-5
K_2SO_3 RECOVERY
232°F
13,950 LB/MIN 1,230 GPM SpG 1.4
J-8 195 BHP 1350 GPM
105°F 212 GPM 1780 LB/MIN SpG 1.0
3780 LB/MIN
FLUE GAS
2220 LB/MIN
F-4 VAPOR-LIQ SEPARATOR 105°F 6'ϕ x 18' 210GPM, 1760 LB/MIN
J-9 5 BHP 360 GPM
WATER 2 GPM 150°F
7.4M ACFM 100°F 35 PSIA
52MM BTU/HR 1250 FT²
C-8
C.W.
VAPOR-LIQUID SEPARATOR
F-3 5'ϕ x 15'
1.6M ACFM 200°F 51% H_2 20% CO 25% CO_2 4% OTHER 2080 LB/MIN
E-2 STRIPPER 7'ϕ x 70' 25 PSIA 250°F
2000 PSIG
TO STACK
BRINK'S MIST ELIMINATOR
L-7
200°F 26M ACFM 960 LB/MIN
C-9 A=300 FT² 22MM BTU/HR INTERNAL COOLING 960 LB/MIN
L-9 REFORMER
122PSIA K.O. DRUM 5'ϕ x 15'
F-9
120°F
500 FT²
1.3 MM BTU HR
C-11
305°F
GPM, 30 LB/MIN
610 GPM 15 PSIG
1.6 M ACFM, 210 LB/MIN 250°F 20 PSIG
1520 LB/MIN
FLASH CHAMBER F-5 8'ϕ x 14'
500 PSIG
200°F 500 PSIA
290 MM BTU/HR
640 MPH 10,800 LB/HR
805 MPH 13,500 LB/HR
NATURAL GAS
500°F 2000 PSIG 0.6M ACFM 47% H_2, 47% CO, 6% OTHER 1980 LB/MIN
REDUCER D-1A&B 520 PSIG 540°F
9'ϕ x 18' EACH
20% $KCHO_2$ 20% K_2CO_3 19% $KHCO_3$
20% $KCHO_2$ 11% K_2CO_3 9% KHS 18% $KHCO_3$
85% $KCHO_2$
J-3 400 GPM 20 BHP
D-2-REGENERATOR 9'ϕ x 60', 2000 PSIG @540°F
J-6 6900 BHP 1600 ACFM SUCTION
J-17 540 BHP/STAGE 2,100 ACFM SUCTION
LB/MIN
7,250 LB/MIN 580 GPM, 20PSIG
5.5M ACFM CO_2 35 PSIA 100°F
STEAM 88M LB/HR
C-7 3800 FT² 88.3MM BTU/HR
2000 PSIG
J-4 640 GPM 1100 BHP

ISSUE ⑤ 5-12-71
ISSUE ④ 4-20-71
ISSUE ③ 4-16-71
ISSUE ② 4-14-71
ISSUE ① 4-5-71

THE M. W. KELLOGG COMPANY
a division of PULLMAN INCORPORATED
SO_2 REMOVAL & RECOVERY
POTASSIUM FORMATE PROCESS

NO.	DESCRIPTION	DATE	BY	CHECKED
7	ADD C-10, 11, & 15, F-8 & 9	5-12-71	W. B.	
6	ADD E-5, C-14, ETC	4-19-71	W.B.	
5	ADD L-10	4-16-71	W.B.	
4	ADD C-12, C-13, F-7, J-19 & CHG. D2	4-13-71	W.B.	
3	GENERAL	3-24-71	W B	
2	GENERAL	3-11-71	W.B.	
1	ADD E-3, E-4 ETC.	2-25-71	W.B.	

REVISIONS

SCALE:
DRAWN:
CHECKED:
APPROVED:
DATED: 2-1-71
ISSUED FOR FABRICATION
ISSUED FOR CONSTRUCTION

CLASS & ITEM	AREA	JOB NUMBER	DRAWING NUMBER
		4092-50	PD-111-D

DRAWING NO.

8A

AMMONIA SCRUBBING ($(NH_4)_2SO_4$ - FERTILIZER)

A. PROCESS

Sulfur Dioxide removal from power plant stack gas by ammonia scrubbing followed by production of ammonium sulfate for use in fertilizer manufacture.

The process under evaluation is designated as Process "A" in the TVA report entitled "Sulfur Oxide Removal From Power Plant Stack Gas, Conceptual Design and Cost Study Series, Study No. 3 Contract No. TV-29233A".

1. Process Description (Refer to MWK Flow Sheet Dwg. No. PD-112-D.

a. Sulfur Dioxide Removal and Production of Ammonium Sulfate

Flue gas exits the air preheater at 300°F and is split into six parallel streams which flow thru identical scrubbing systems before being exhausted into a common stack. The gas is first cooled to 172°F in gas cooler C-1. Ammonia is injected into the gas stream upstream of the cooler to neutralize SO_3 for corrosion prevention in the lower part of the scrubber. The cooled gas containing 4.9 gr/scf of solid particulates is scrubbed with water on the bottom tray of a four stage scrubbing tower E-1. 99.5 wt % of the solids are removed and discharged to settling tank F-4 common to the six scrubbers. The solids are settled out and diluted with water to a 12 wt % ash slurry which is pumped to a settling pond. The solids free gas flows countercurrent to the wash solution containing NH_3, SO_2, $(NH_4)_2SO_3$, NH_4HSO_3 and $(NH_4)_2SO_4$. Three stages are required to remove 90 wt % of the SO_2 by reaction with NH_3 and $(NH_4)_2SO_3$. The proposed scrubbers are countercurrent seive tray type Impinjet gas scrubbers manufactured by the W. W. Sly Mfg. Co.

Six scrubbers are required to handle the flue gas from a 1000 MW plant since the largest scrubber available is 20' wide x 40' long. The total sidestream drawoff from each of the three wash trays is segregated flowing respectively to the recirculation surge tanks F-1, 2, 3. Each tank is common to three scrubbers resulting in two recirculation systems each of which feeds three scrubbers via pumps J-1, 2, 3. Fresh NH_3 makeup is added to each recirculation stream and the liquid composition on the trays is regulated by drawing off a slipstream from each drum flowing stepwise from F-3 to F-2 to F-1. The scrubber effluent product is withdrawn from drums F-1A, B and pumped to a common surge tank F-6. The scrubber effluent consists of a 50 wt % salt solution containing a mixture of SO_2, NH_3 and ammonium sulfite, bisulfite and sulfate. The flue gas is cooled adiabatically in the scrubber by the evaporation of water and leaves the scrubber saturated at 116°F. Makeup water is injected into the scrubber above the top tray and liquid entrainment is removed by a fixed blade impingement baffle located in the top of the scrubber. The gas is reheated to 247°F in gas reheater C-2 to ensure adequate dispersion of the gas leaving the stack. Flow through scrubbers is maintained by exhaust fan J-9 located downstream of gas reheater C-2. The six fans exhaust to a common stack and maintain the entire system under slight negative pressure. A pumparound system utilizing surge tank F-5 and pump J-8 pumps tempered water thru cooler C-1 and gas reheater C-2 in series transferring heat from C-1 to C-2.

The combined effluent product from the six scrubbers is pumped from surge tank F-6 to neutralizer D-1. The neutralizer is sparged with NH_3 to convert the remaining bisulfite to sulfite in order to minimize SO_2 loss during the subsequent oxidation reaction. Water is added to the neutralizer to lower the salt concentration to 40 wt % to prevent crystallization of ammonium sulfate in the oxidizer. Off-gas from the neutralizer containing ammonia and water is vented back to the scrubbers. The neutralized solution is pumped to oxidizers D-2A, B (2 in parallel) where the ammonium sulfite is reacted with air at 100 psig and 185°F to produce ammonium sulfate. Heat of reaction is removed by recirculating thru solution cooler C-4 where the salt solution is cooled from 185°F to 135°F. About

8 vol % of the cooled salt solution is pumped to surge tank F-7 from which it is fed to the fertilizer plant precipitator. Off-gas from the oxidizers containing nitrogen, excess oxygen and water is vented back to the scrubbers.

b. Production of Ammonium Nitrate-Phosphate Fertilizer

Phosphate rock is reacted with 60% nitric acid to form soluble calcium nitrate and phosphoric acid. The resulting extract slurry is heated to 165°F and charged to the precipitator where it reacts with ammonium sulfate to form insoluble $CaSO_4$, H_3PO_4 and NH_4NO_3. The $CaSO_4$ is removed by filtration and discharged to a sluice tank where it is diluted with water to a 20 wt % slurry and pumped to the settling pond. The filtrate consisting mainly of ammonium nitrate and phosphoric acid is neutralized with ammonia and then concentrated to 99.7 wt % in a steam heated falling film type evaporator. The concentrated ammonium nitrate-phosphate product is spray dried with air in a prilling tower, cooled, screened for particle size control and sent to bulk product storage. Undersize and oversize product is dissolved and slurried and recycled to the neutralizer feed tanks. Total production is 2370 tons/day of fertilizer ranging in content from 25-15-0 to 28-14-0 (N_2, P_2O_5, Potash) depending on the type of phosphate rock used as feed and the plant operating conditions. 60% nitric acid used in the extraction reaction is produced in a 1275 T/D (100% HNO_3 basis) acid plant. Ammonia storage, unloading and pumping facilities are provided to supply the acid plant, fertilizer plant, SO_2 scrubber and bisulfite neutralizer requirements.

2. Process Design Basis

Basic process design criteria common to all of the SO_2 removal processes being evaluated are not included in the following list.

Overall Plant Capacity Factor, % of Nameplate Rating	
1st to 10th year	80%
11th to 15th "	57%
16th to 20th "	40%
21st to 35th "	17%
Average Capacity Factor	43%

a. Ammonia Scrubbers E-1A, B, C, D, E, F

The following data pertaining to the scrubbers selected as being most suitable for this service was obtained from the W. Sly Mfg. Co. bulletin and is applicable to the cross flow sieve tray Impinjet type gas scrubber.

Quantity (6) Six
Dimensions 20' x 40' (rect.) x 27' high
Design Gas Velocity, Nor. 420 fpm, max. 500 fpm, actual 461 fpm
Fly Ash Dust Removal 99.5% (total fly ash from boiler)
Water recirculation to bottom scrubber stage for dust removal, combined plate and spray water, 3 gpm/1000 ACFM gas
Ammonia injection upstream of gas cooler C-1 for corrosion control in bottom of scrubber is based on the stoichiometric quantity required to react with the 2% of sulfur in coal which forms SO_3.

b. Scrubber Operating Conditions

Gas inlet temp., 172°F
Gas outlet temp.,116°F
Effluent temp., 120°F
Effluent salt concentration, 50 wt %
Effluent NH_3:S mole ratio, 1.49
Salt solution recirculation rate, 1.14 gpm/1000 ACFM
Fly Ash Slurry concentration to settling pond, 12 wt % solids

c. Bisulfite Neutralizer D-1

Salt inlet temp., 120°F
Salt outlet temp., 188°F
Effluent salt concentration, 40 wt %
Effluent NH_3:S mole ratio, 2.0
Approx. retention time, 10 minutes

d. Sulfite Oxidizer D-2A, B

Salt inlet temp, 188°F
Salt outlet temp.,185°F
Recirculated salt solution temp., 135°F
Operating temp., 185°F
Air to liquid ratio, 7.6 SCF/gal
Operating pres., 100 psig

pH, 6.5
Approx. retention time, 1 hr
Recirculated salt solution to product ratio, 11:1

e. Ammonium Nitrate - Phosphate Fertilizer Plant, L-2

Plant Capacity (25-15-0 to 28-14-0 Range), 2370 Tons/CD
Precipitator Effluent Temp., 150°F
Filter Effluent Temp., 100°F
Neutralizer Effluent Temp., 150°F
Evaporator Salt Concentration (28-14-0), 99.7 wt %
Prilling Tower Recycle Ratio, lb Recycle/lb Product, 1:4
Neutralizer NH_3:H_3PO_4 mole ratio, 1.37

f. Nitric Acid Plant, L-1

Capacity (100% HNO_3 Basis), 1276 T/CD
Capacity (60% " "), 2126 T/CD

g. Miscellaneous Storage Facilities

Liquid Ammonia Storage (10 days consumption), 2,765,000 gal
(insulated atmos pres. storage @ -28°F)
Phosphate rock storage (2 days consumption), 2500 Tons
60% Nitric Acid Storage (2 days production), 750,000 gal
Fertilizer Product bulk storage (90 days production), 215,000 Tons

h. Settling Pond

Basis: 10 years combined production of gypsum and recovered fly ash

Fly Ash	3096 Acre-Feet
Gypsum	4644 " "

3. Process Design Rationale

The TVA report discussed three alternate methods for the production of the intermediate product, ammonium sulfate. These are complete oxidation of the sulfite and bisulfite products to sulfate in the scrubber proper, external oxidation of the scrubber effluent in a separate vessel and acidification of the scrubber effluent with H_2SO_4. Some production of sulfate occurs in the scrubber and the various factors which inhibit or promote the production of sulfate have not been fully evaluated. This reaction does tie up ammonia in the system thereby reducing the efficient removal of SO_2.

In view of the many unanswered questions and lack of experimental data this procedure was not considered to be a workable system at this time, however it is planned to evaluate partial oxidation in the scrubber up to an optimum point to minimize the size of the external oxidation vessel.

Production of ammonium sulfate by acidification with H_2SO_4 was discussed from the standpoint of the pilot plant work done by TVA and the commercial scale operation of Cominco, however no definite reason was given for not using this method. Presumably oxidation in a separate vessel was chosen as the preferred method for producing $(NH_4)_2SO_4$ primarily because this method has been proven commercially in Japan and complete details for carrying out this reaction are available under license from the Japanese Engineering Consulting Co. (JECCO). A fourth method which has potential and which will be evaluated is the crystallization, by cooling, of $(NH_4)_2SO_4$ from a scrubber sidestream.

The technology involved in the production of ammonium nitrate-phosphate fertilizer from $(NH_4)_2SO_4$, phosphate rock and HNO_3 has been well established both in the U.S. and Europe therefore further evaluation was not considered to be necessary to carry out this study. Various types of scrubbers were looked at including packed, venturi, spray, mobile bed, orifice and sieve tray towers. The selection was made on the basis of the following criteria;

(a) an overall pressure drop less than 12" H_2O at 90% SO_2 absorption.

(b) High efficiency particulate removal, minimum 99.5%.

(c) resistant to plugging by solids in the gas stream.

(d) a high turndown ratio.

(e) adaptable to stagewise contacting of gas and liquid with complete segreation of each recirculation stream to permit controlling NH_3 concentration on each tray for the purpose of minimizing NH_3 loss. This requirement was considered to be the single most important criterion.

The crossflow sieve tray (impingement type) appeared to meet these basic requirements better than the other tower types investigated. Further this type of scrubber is available in the large size required for 500 and 1000 MW power plants which is not the case for a number of the tower types investigated. The plugging problems experienced with this type of scrubber in the wet limestone SO_2 removal process which involves injecting a limestone slurry on the top tray apparently do not arise in the NH_3 system since essentially all solids in the gas stream are removed on the bottom tray with water sprays. This type of scrubber is normally supplied with a fixed vane type mist remover. The entrainment removal efficiency of this type of demister is low compared to wire mesh or fiber bed demisters. Therefore if provisions are made to prevent plugging the latter type of demister may be more effective in removing entrained salts which could possibly cause trouble in the gas reheater or exhaust fan.

A cost comparison was made of five methods for cooling and reheating the flue gas. The indirect liquid to gas system proved to be the lowest priced in terms of $/ton of coal burned. The TVA pilot plant study of NH_3 scrubbing involved use of a 2'ϕ x 10' high packed tower. Variables studied were circulation rate, pH, solution concentration, packing depth and gas velocity. The results of these tests plus data obtained from articles published by Johnstone, Chertkov and others provided the design basis for the scrubber used in this study. Further pilot plant evaluation is required to firm up the optimum scrubbing variables including scrubber type, gas velocity, mist remover type, inlet gas temperature and the point of NH_3 addition.

4. Process Design Appraisal

This process which combines NH_3 scrubbing with fertilizer production was designed to determine the economic potential of a recovery type process as applied to SO_2 removal processes. Process "A" which shows the best economics of the three processes evaluated does not offer a very attractive investment potential. Since it is known that plant cost estimates increase substantially as engineering becomes more definitive it is reasonable to predict that the rate of return or payout for this process based on a more definitive engineering study would be even less attractive than that shown in the TVA report. This approach does point up the relative difficulty in attempting to fit any type of recovery scheme whether the end product is sulfur, sulfuric acid or fertilizer into the general economy without disrupting the existing supply demand pattern. In the process under evaluation the fertilizer plants would have to be located in the midwest area of the U.S. where marketing conditions are most favorable. The number of such plants would need to be limited to 2 or 3, 500 MW plants in order not to over saturate the existing fertilizer market so that even under the most favorable conditions this process has very limited applicability.

The ammonia scrubbing process is a relatively cheap and effective method for removing SO_2 from flue gas. It has a high absorption efficiency and requires fairly simple handling techniques in the scrubbing and regeneration steps. A disadvantage of this process which is common to all of the wet scrubbing processes is that the flue gas must be cooled and reheated.

As compared to limestone,ammonia is expensive and therefore must either be regenerated for recycle or become a constituent of a saleable product. In the process under evaluation all of the nitrogen remains in the product resulting in a fertilizer with a high nitrogen to phosphate ratio. This type of fertilizer has a lower market demand than fertilizers with lower nitrogen to phosphate ratios.

The ammonia scrubbing process is well developed and has been tested extensively in Russia, Japan and France. However it is still felt that substantial additional pilot plant testing is justified to optimize the operating variables of the process. TVA currently plans to evaluate, (a) the degree of oxidation taking place in the scrubber and the variables which affect oxidation, (b) optimum bisulfite/sulfite ratio for best scrubber efficiency, (c) determination of how much dust can be tolerated in the subsequent oxidation and fertilizer production steps, (d) steady state composition of the scrubber liquor and the effect of dissolved solids buildup on scrubber operation, (e) pH control for corrosion prevention.

The oxidation reaction and the fertilizer plant and auxiliary plants represent established technology proven on a commercial basis and therefore do not require further evaluation.

The nitric acid plant required for a 1000 MW power plant has a capacity of 1276 T/CD (100% HNO_3 Basis). The ammonia required for the combined scrubbing operation and nitric acid plant is 716 T/CD. This amount of NH_3 would normally be produced on site rather than being shipped in by rail. This consideration may place some further restriction on the location of a plant of this type.

B. CHEMISTRY

The chemistry associated with the ammonia scrubbing process, for sulfur dioxide removal from stack gas, falls into three separate categories, namely:

- (a) absorption
- (b) recovery
- (c) production of finished product.

(a) In the first of these, sulfur oxides are removed from the stack gas by absorption into a concentrated aqueous solution of ammonium sulfite. The chemical reaction shown in equation 1 describes the principle chemistry of the scrubbing process.

$$(NH_4)_2SO_3 + SO_2 + H_2O = 2\ NH_4HSO_3 \qquad \text{(equation 1)}$$

Detailed and reliable thermodynamic and kinetic data are available for this system. These are sufficient for adequate definition of the process parameters as well as for selection of optimum conditions for most efficient sulfur dioxide removal. Equilibrium data indicate that CO_2, present as a major component in stack gas, can not effectively interfere with the efficiency of the SO_2 removal. Variations of SO_2 partial pressure with temperature, solution pH and solution concentration have been measured and accurate data are available.

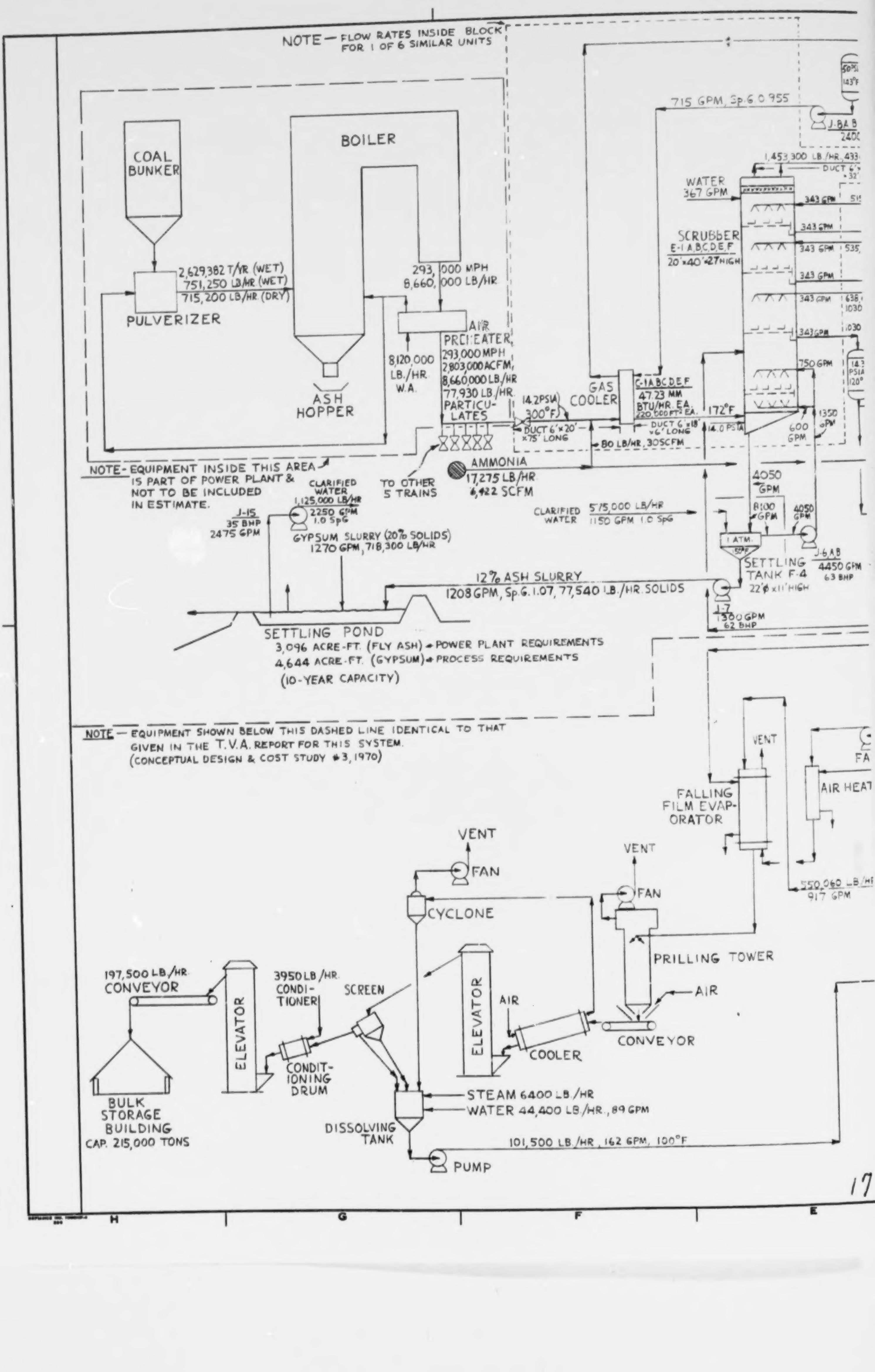
(b) The recovery of sulfur values from the spent scrubber solution can be accomplished in several ways. The method of choice depends almost entirely on the type of end product desired. For example, when sulfuric acid is the end product, a regenerative process can be used that essentially comprises the reversal of the scrubbing reaction (equation 1) by means of air stripping at elevated temperature. Regenerated solution is recycled to the scrubber and the sulfur dioxide is used as feedstock to a sulfuric acid plant. In situ oxidation (equation 2) must be held to a minimum for regenerative operation as

$$2(NH_4)_2SO_3 + O_2 = 2(NH_4)_2SO_4 \qquad \text{(equation 2)}$$

this represents a net loss in scrubbing capacity. Chemical factors required to control the extent of this reaction are known.

When ammonium sulfate is the desired recovery product, the oxidation reaction (equation 2) must be carried out in a vessel separate from that employed in the scrubbing operation since conditions that favor equations 1 and 2 are mutually incompatible.

(c) The chemistry involved in the production of the finished product depends entirely on the nature of the end product. However, for those cases where fertilizer materials are to be produced, all of the required chemistry is well known in the art.

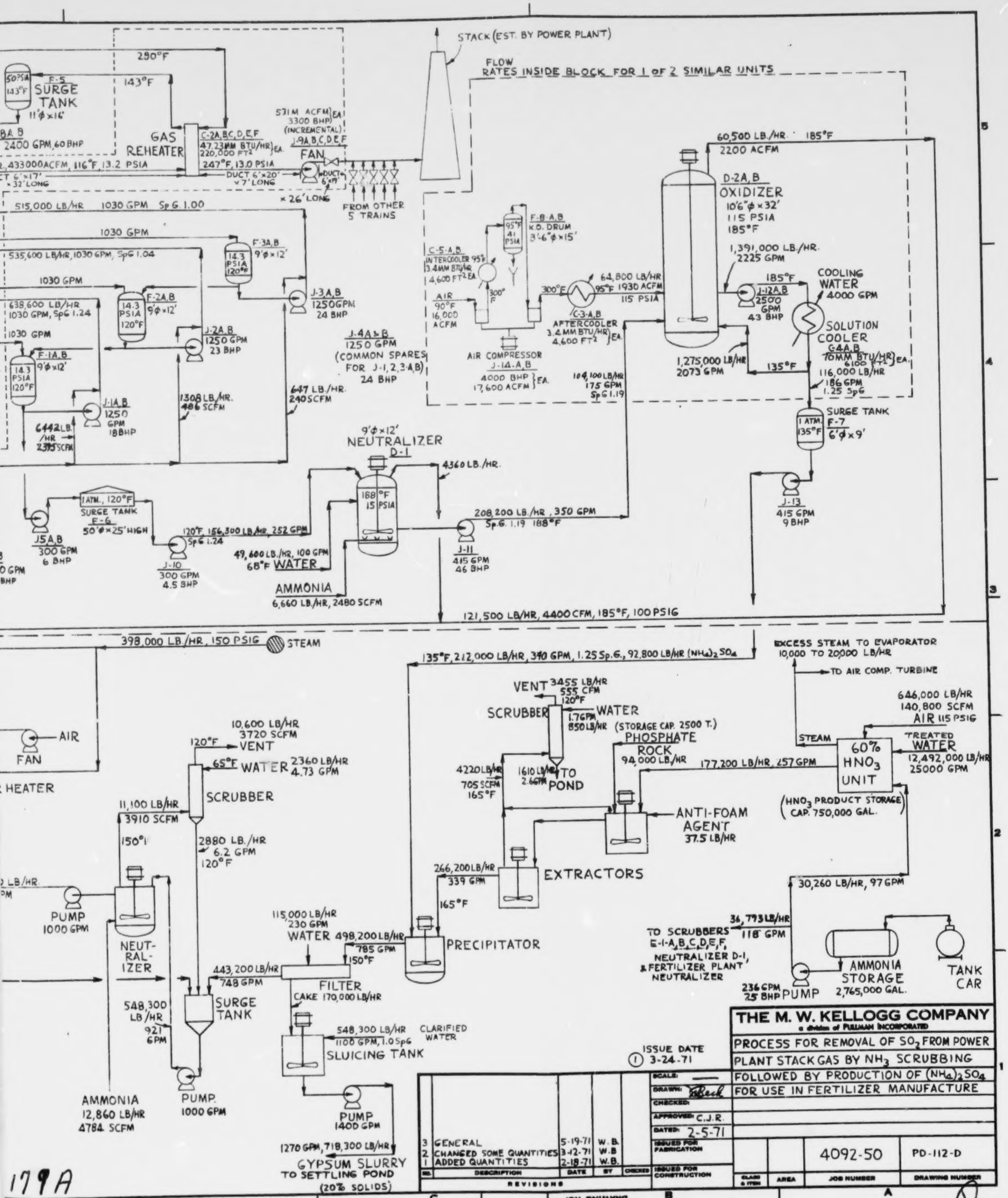

NOTE — FLOW RATES INSIDE BLOCK FOR 1 OF 6 SIMILAR UNITS

NOTE - EQUIPMENT INSIDE THIS AREA IS PART OF POWER PLANT & NOT TO BE INCLUDED IN ESTIMATE.

NOTE — EQUIPMENT SHOWN BELOW THIS DASHED LINE IDENTICAL TO THAT GIVEN IN THE T.V.A. REPORT FOR THIS SYSTEM. (CONCEPTUAL DESIGN & COST STUDY #3, 1970)

COAL BUNKER
BOILER
2,629,382 T/YR (WET)
751,250 LB/HR (WET)
715,200 LB/HR (DRY)
PULVERIZER
293,000 MPH
8,660,000 LB/HR
AIR PREHEATER,
293,000 MPH
2,803,000 ACFM,
8,660,000 LB./HR
77,930 LB./HR. PARTICULATES
8,120,000 LB./HR W.A.
ASH HOPPER
14.2PSIA
300°F
DUCT 6'×20' ×75' LONG
GAS COOLER
C-1ABCDEF
47.23 MM BTU/HR. EA.
220,000 FT² EA.
DUCT 6'×18' ×6' LONG
80 LB/HR, 30SCFM
172°F
14.0 PSIA
715 GPM, Sp.G. 0.955
50PSI
143°F
J-BA B
2400
1,453,300 LB./HR., 433
DUCT 6'
×32'
WATER 367 GPM
SCRUBBER E-1 A,B,C,D,E,F 20'×40'×27'HIGH
343 GPM
343 GPM
343 GPM
343 GPM
343 GPM
343 GPM
515
535,
638,
1030
1030
750 GPM
1350 GPM
600 GPM
14.
PSIA
120°
TO OTHER 5 TRAINS
AMMONIA 17,275 LB/HR 6,422 SCFM
CLARIFIED WATER 1,125,000 LB/HR 2250 GPM 1.0 SpG
J-15 35 BHP 2475 GPM
GYPSUM SLURRY (20% SOLIDS) 1270 GPM, 718,300 LB/HR
CLARIFIED WATER 575,000 LB/HR 1150 GPM 1.0 SpG
4050 GPM
8100 GPM
4050 GPM
1 ATM.
150°F
SETTLING TANK F-4 22'ϕ×11'HIGH
J-6,AB 4450 GPM 63 BHP
12% ASH SLURRY 1208 GPM, Sp.G. 1.07, 77,540 LB./HR. SOLIDS
J-7 1300 GPM 62 BHP
SETTLING POND
3,096 ACRE-FT. (FLY ASH) ← POWER PLANT REQUIREMENTS
4,644 ACRE-FT. (GYPSUM) ← PROCESS REQUIREMENTS
(10-YEAR CAPACITY)
VENT
FALLING FILM EVAPORATOR
VENT
FA
AIR HEAT
550,060 LB./HR
917 GPM
VENT
FAN
CYCLONE
VENT
FAN
PRILLING TOWER
AIR
CONVEYOR
COOLER
AIR
ELEVATOR
SCREEN
3950 LB./HR. CONDITIONER
CONDITIONING DRUM
ELEVATOR
197,500 LB./HR. CONVEYOR
BULK STORAGE BUILDING CAP. 215,000 TONS
STEAM 6400 LB./HR
WATER 44,400 LB./HR., 89 GPM
DISSOLVING TANK
PUMP
101,500 LB./HR, 162 GPM, 100°F
H
G
F
E

A



STACK (EST. BY POWER PLANT)
FLOW RATES INSIDE BLOCK FOR 1 OF 2 SIMILAR UNITS
250°F
143°F
50 PSIA 143°F
F-5 SURGE TANK 11'ϕ×16'
2400 GPM, 60 BHP
GAS REHEATER
C-2A,B,C,D,E,F 47.23 MM BTU/HR 220,000 FT² EA.
531 M ACFM 3300 BHP (INCREMENTAL) EA.
J-9A,B,C,D,E,F FAN
2,433000 ACFM, 116°F, 13.2 PSIA
247°F, 13.0 PSIA
DUCT 6'×20' ×7' LONG
DUCT 6'×17' ×32' LONG
DUCT 6'×17' ×26' LONG
FROM OTHER 5 TRAINS
515,000 LB/HR 1030 GPM Sp G 1.00
1030 GPM
535,600 LB/HR, 1030 GPM, SpG 1.04
F-3A,B 14.3 PSIA 120°F 9'ϕ×12'
1030 GPM
J-3A,B 1250 GPM 24 BHP
638,600 LB/HR 1030 GPM, SpG 1.24
F-2A,B 14.3 PSIA 120°F 9'ϕ×12'
J-2A,B 1250 GPM 23 BHP
1030 GPM
F-1A,B 14.3 PSIA 120°F 9'ϕ×12'
J-1A,B 1250 GPM 18 BHP
6442 LB/HR 2395 SCFM
1308 LB/HR 486 SCFM
647 LB/HR 240 SCFM
J-4A & B 1250 GPM (COMMON SPARES FOR J-1,2,3-A,B) 24 BHP
C-5-A,B INTERCOOLER 95°F 3.4 MM BTU/HR 4,600 FT² EA.
F-8-A,B K.O. DRUM 95°F 41 PSIA 3'-6"ϕ×15'
AIR 90°F 16,000 ACFM
300°F
AIR COMPRESSOR J-14-A,B 4000 BHP 17,600 ACFM EA.
300°F 95°F
64,800 LB/HR 1930 ACFM 115 PSIA
C-3-A,B AFTERCOOLER 3.4 MM BTU/HR 4,600 FT² EA.
104,100 LB/HR 175 GPM SpG 1.19
60,500 LB/HR 185°F 2200 ACFM
D-2A,B OXIDIZER 10'6"ϕ×32' 115 PSIA 185°F
1,391,000 LB/HR 2225 GPM
185°F
J-12A,B 2500 GPM 43 BHP
COOLING WATER 4000 GPM
SOLUTION COOLER G4A,B 70MM BTU/HR 6100 FT² EA.
1,275,000 LB/HR 2073 GPM
135°F
116,000 LB/HR 186 GPM 1.25 SpG
SURGE TANK F-7 1 ATM. 135°F 6'ϕ×9'
J-13 415 GPM 9 BHP
9'ϕ×12' NEUTRALIZER D-1 188°F 15 PSIA
4360 LB/HR
1 ATM., 120°F SURGE TANK F-6 50'ϕ×25' HIGH
J5A,B 300 GPM 6 BHP
120°F 156,300 LB/HR, 252 GPM SpG 1.24
J-10 300 GPM 4.5 BHP
208,200 LB/HR, 350 GPM SpG 1.19 188°F
J-11 415 GPM 46 BHP
49,600 LB/HR, 100 GPM 68°F WATER
AMMONIA 6,660 LB/HR, 2480 SCFM
121,500 LB/HR, 4400 CFM, 185°F, 100 PSIG
398,000 LB/HR, 150 PSIG STEAM
135°F, 212,000 LB/HR, 340 GPM, 1.25 Sp.G., 92,800 LB/HR (NH4)2SO4
EXCESS STEAM TO EVAPORATOR 10,000 TO 20,000 LB/HR
TO AIR COMP. TURBINE
AIR FAN
HEATER
10,600 LB/HR 3720 SCFM
120°F VENT
65°F WATER 2360 LB/HR 4.73 GPM
SCRUBBER
11,100 LB/HR 3910 SCFM
150°F
2880 LB/HR 6.2 GPM 120°F
LB/HR
PUMP 1000 GPM
NEUTRALIZER
548,300 LB/HR 921 GPM
SURGE TANK
PUMP 1000 GPM
AMMONIA 12,860 LB/HR 4784 SCFM
VENT 3455 LB/HR 555 CFM 120°F
SCRUBBER
WATER 1.76 GPM 850 LB/HR
(STORAGE CAP. 2500 T.)
PHOSPHATE ROCK 94,000 LB/HR
4220 LB/HR 705 SCFM 165°F
1610 LB/HR 2.6 GPM TO POND
ANTI-FOAM AGENT 37.5 LB/HR
266,200 LB/HR 339 GPM
EXTRACTORS
165°F
115,000 LB/HR 230 GPM WATER
498,200 LB/HR 785 GPM 150°F
PRECIPITATOR
443,200 LB/HR 748 GPM
FILTER
CAKE 170,000 LB/HR
548,300 LB/HR 1100 GPM, 1.0 SpG CLARIFIED WATER
SLUICING TANK
PUMP 1400 GPM
1270 GPM, 718,300 LB/HR
GYPSUM SLURRY TO SETTLING POND (20% SOLIDS)
177,200 LB/HR, 257 GPM
STEAM
60% HNO3 UNIT
646,000 LB/HR 140,800 SCFM AIR 115 PSIG
TREATED WATER 12,492,000 LB/HR 25000 GPM
(HNO3 PRODUCT STORAGE CAP. 750,000 GAL.)
30,260 LB/HR, 97 GPM
36,793 LB/HR 118 GPM
TO SCRUBBERS E-1-A,B,C,D,E,F, NEUTRALIZER D-1, & FERTILIZER PLANT NEUTRALIZER
236 GPM 25 BHP PUMP
AMMONIA STORAGE 2,765,000 GAL.
TANK CAR
5
4
3
2
1
D
C
B
A
DRAWING NO.

ISSUE DATE
① 3-24-71

THE M. W. KELLOGG COMPANY
a division of PULLMAN INCORPORATED

PROCESS FOR REMOVAL OF SO_2 FROM POWER PLANT STACK GAS BY NH_3 SCRUBBING FOLLOWED BY PRODUCTION OF $(NH_4)_2SO_4$ FOR USE IN FERTILIZER MANUFACTURE

SCALE:
DRAWN: E.Beck
CHECKED:
APPROVED: C.J.R.
DATED: 2-5-71
ISSUED FOR FABRICATION
ISSUED FOR CONSTRUCTION

CLASS & ITEM	AREA	JOB NUMBER	DRAWING NUMBER
		4092-50	PD-112-D

REVISIONS

NO.	DESCRIPTION	DATE	BY	CHECKED
3	GENERAL	5-19-71	W.B.	
2	CHANGED SOME QUANTITIES	3-12-71	W.B.	
1	ADDED QUANTITIES	2-18-71	W.B.	

179A

B

AMMONIA SCRUBBING (ALTERNATE A)

(STEAM STRIPPING REGENERATION)

A. PROCESS

Sulfur dioxide removal from power plant stack gas by scrubbing ith ammonia followed by regeneration by stripping and production sulfur dioxide for use in sulfuric acid manufacture.

1. Process Description (Refer to MWK Flow Sheet Dwg. No. PD-113-D)

a. Sulfur Dioxide Removal from Flue Gas

Flue gas exits the air preheater at 300°F and is split into six parallel streams which flow through identical scrubbing systems before being exhausted into a common stack. The gas is first cooled to 172°F in gas cooler C-1. The cooled gas containing 4.9 gr/scf of solid particulates is scrubbed with water on the bottom tray of a four-stage scrubbing tower E-1. 99.5 wt % of the solids are removed and discharged to settling tank F-4 common to the six scrubbers. The solids are settled out and diluted with water to a 12 wt % ash slurry which is pumped to a settling pond. The solids-free gas flows countercurrent to the wash solution containing NH_3, SO_2, $(NH_4)_2SO_3$, NH_4HSO_3 and $(NH_4)_2SO_4$. Three stages are required to remove 90 wt % of the SO_2 by reaction with NH_3 and $(NH_4)_2SO_3$. The proposed scrubbers are countercurrent sieve tray type Impinjet gas scrubbers manufactured by the W. W. Sly Mfg. Co.

Six scrubbers are required to handle the flue gas from a 1000 MW plant since the largest scrubber available is 20' wide x 40' long. The total sidestream drawoff from each of the three wash trays is segregated, flowing respectively to the recirculation surge tanks F-1, 2, 3. Each tank is common to three scrubbers resulting in two recirculation systems each of which feeds three scrubbers via pumps J-1, 2, 3. Fresh NH_3 makeup is added to each recirculation stream and the liquid composition on the trays is regulated by drawing off a slipstream from each drum flowing stepwise from F-3 to F-2 to F-1. The scrubber effluent product is withdrawn from drums F-1A, B and pumped to regenerator E-2. The scrubber effluent consists of 48 wt % salt solution containing a mixture of SO_2, NH_3 and ammonium sulfite, bisulfite and sulfate. The flue gas is cooled adiabatically in the scrubber by the evaporation of water and leaves the scrubber saturated at 116°F. Makeup water is injected into the scrubber above the top tray and liquid entrainment is removed by a fixed blade impingement baffle located in the top of the scrubber. The gas is reheated to 247°F in gas reheater C-2 to ensure adequate dispersion of the gas leaving the stack. Flow through the scrubbers is maintained by exhaust fan J-9 located downstream of gas reheater C-2. The six fans exhaust to a common stack and maintain the entire system under slight negative pressure. A pumparound system utilizing surge tank F-5 and pump J-8 circulates tempered water through cooler C-1 and gas reheater C-2 in series transferring heat from C-1 to C-2.

b. Regeneration of Scrubber Effluent and Production of Sulfur Dioxide

The combined scrubber effluent from the six scrubbers is pumped from tanks F-1A&B through preheaters C-4 and C-7, where it is heated to 185°F and discharged into the top of Regenerator E-2. The regenerator is a packed column operated under vacuum at 185°F and 348 MMHg (absolute pressure) with an external steam heated thermosiphon reboiler providing the vapor boilup. The feed contains a mixture of $(NH_4)_2SO_3$, NH_4HSO_3 and $(NH_4)_2SO_4$ in aqueous solution with an S/C* ratio of 0.85. The unstable NH_4HSO_3 breaks down when heated releasing NH_3 and SO_2. These gases along with water vapor are carried overhead. The regenerated stripper bottoms leave at 187°F with an S/C ratio of 0.76. A slipstream comprising 2.8% of the regenerator effluent is pumped to the sulfate reactor D-1 where it is reacted with $CaCO_3$ to form NH_3, CO_2 and $CaSO_4$. This removes the net make of $(NH_4)_2SO_4$ produced in the scrubber. The reactor off gas consisting of NH_3, CO_2 and H_2O vapor is cooled to 120°F in C-6 where part of the water condenses and returns to the reactor. The remaining vapors are recycled back to the scrubber via the sidestream recirculation circuits. The insoluble $CaSO_4$ settles out and is pumped to sluice tank F-8 where it is diluted with water to a 20 wt % slurry. It is then pumped to the settling pond. The balance of the regenerator effluent is cooled to 120°F in C-8 and recycled back to the scrubber recirculation drums F-1, 2, 3.

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* $\frac{S}{C} = \frac{\text{MOLES SULFUR}}{\text{MOLES AMMONIA}}$ (contained in $(NH_4)_2SO_3$ and NH_4HSO_3 only)

The regenerator overhead vapors are partially condensed in C-4 which exchanges heat with the cold scrubber effluent. Essentially all of the NH_3 vapors condense in C-4 along with SO_2 to form a weak aqueous solution of $(NH_4)_2SO_3$. The condensate discharges to seal drum F-6 from which it is pumped into the regenerator effluent stream and then recycled back to the scrubber. The remaining vapors are cooled to 122°F in C-5 to condense the bulk of the water vapors. Approximately 8.5% of the SO_2 condenses along with the water and is collected in seal drum F-7. The remaining vapor which contains 90 wt % SO_2 is pumped via vacuum pump J-15 to a sulfuric acid production unit. The condensate collected in drum F-7 is pumped to stripper E-3 where the SO_2 is stripped out with compressed air and discharged to the sulfuric acid production unit. Total SO_2 recovery is 15, 190 lb/hr in terms of sulfur equivalent representing 68.8% of the sulfur removed from the flue gas.

2. Process Design Basis

Basic process design criteria common to all of the SO_2 removal processes being evaluated are not included in the following list.

Overall Plant Capacity Factor, % of Nameplate Rating

1st to 10th year	80%
11th to 15th year	57%
16th to 20th year	40%
21st to 35th year	17%
Average Capacity Factor	43%

a. Ammonia Scrubbers E-1A, B, C, D, E, F

The following data pertaining to the scrubbers selected as being most suitable for this service was obtained from the W. Sly Mfg. Co. bulletin and is applicable to the cross flow sieve tray impinjet type gas scrubber.

Quantity (6) Six
Dimensions 20' x 40' (rect.) x 27' high
Design Gas Velocity, Nor. 420 fpm, max. 500 fpm, actual 461 fpm
Fly Ash Dust Removal 99.5% (total fly ash from boiler)
Water recirculation to bottom scrubber stage for dust removal
Combined plate and spray water, 3 gpm/1000 ACFM gas

b. Scrubber Operating Conditions

Gas inlet temp., 172°F
Gas outlet temp., 116°F
Effluent temp., 120°F
Effluent salt concentration, 48 wt %
Effluent $S:NH_3$ mole ratio, S/C = 0.85
Salt solution recirculation rate, 1.06 gal/min-ft^2
Fly ash slurry concentration to settling pond, 12 wt % solids

c. Regenerator E-2

Liquid inlet temp., 185°F
Liquid outlet temp., 187°F
Tower top abs. pres. 348 MMHg
Tower Bottom abs. pres. 363 MMHg
Feed composition, $(S/C)_i = 0.85$
Effluent composition, $(S/C)_F = 0.76$
Theoretical stages, 5
Liquid flow rate L, 1.15 lb/sec-ft^2
Gas flow rate G, 0.26 lb/sec-ft^2
Packing type, 3" Intalox saddles

d. Sulfate Reactor, D-1

Operating temp., 187°F
Operating Pres., 18 psia
Retention Time, 30 minutes

e. SO_2 Stripper, E-3

Oper. Temp., 120°F

Oper. Pres., 5 psig

Pres. drop thru internals, 0.25 psi

Stripping medium, air (8 moles air/mole SO_2)

Packing type, 2" Intalox saddles

Liquid flow rate L, 7.1 $lb/sec\text{-}ft^2$

Gas flow rate G, 0.315 $lb/sec\text{-}ft^2$

f. Settling Pond L-1

Basis: 10 years combined production of gypsum and recovered fly ash.

Fly ash, 3096 acre-ft

Gypsum, 854 acre-ft

3. Process Design Rationale

The scrubbing operation, with proper modification of operating conditions, is assumed to be capable of producing an effluent with an S/C ratio of 0.85 using the three stage scrubber selected for the TVA base case. Literature references indicate that a ratio of 0.92 or higher is attainable. If true this would enhance the regeneration aspects of the process and show a more profitable overall operation. Scrubbing liquid sidestream recirculation rates are based on the test data of Chertkov reproduced in the TVA report (1). This data was obtained from a 6 plate sieve tray absorber with an effluent S/C ratio of 0.90. A sulfate make of 15% of the total sulfur absorbed was assumed to be constant for all sulfate concentrations in the recirculation liquid. Since the production of sulfate involves a simple oxidation reaction this should be a reasonably accurate assumption.

The stripper design is based on the Johnstone vapor pressure formulas for NH_3, SO_2 and H_2O over an aqueous sulfite, bisulfite solution. The Russian references claim that the Johnstone formulas predict higher than actual steam consumption rates in the stripper.

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(1) "Sulfur Dioxide Removal From Power Plant Stack Gas, Ammonia Scrubbing", Conceptual Design and Cost Series Study No. 3, 1970, Contract No. TV 29233A.

Since we cannot reconcile these two methods of predicting vapor pressure we have retained the Johnstone method as given in the TVA base case report. The theoretically possible separation value (limiting S/C ratio) attainable in the stripper and the practically attainable separation based on temperature and number of transfer units were calculated by the method of Gordeev and Chertkov (2). Calculations made to find rough optimum operating conditions indicated that 85°C was better than 95°C (stripper top temperature) for the assumed feed composition and that five stages gives maximum separation efficiency. The final design is based on tower top conditions of 85°C at 348 MMHg absolute pressure using a packed column with 5 theoretical stages.

The net sulfate make is removed by reacting with $CaCO_3$ to form $CaSO_4$ which is discarded and NH_3 which is recycled to the scrubber. Since the stripper effluent contains a mix of sulfite, bisulfite and sulfate some quantity of sulfite and bisulfite will be reacted along with the sulfate thereby adding to the total sulfur throwaway. The quantity of sulfur lost in this manner can be arbitrarily set by fixing the sulfate/sulfite-bisulfite ratio and consequently the circulation rate. Taking the relative value of the sulfate/sulfite-bisulfite ratio as 1/1 at a zero recirculation rate gives a net sulfur recovery of 10% of the total absorbed. A ratio of 5/1 results in a recovery of about 69% and a 10/1 ratio in 76% recovered. The 5/1 ratio is about optimum since further increases in sulfur recovery result in a disproportionate increase in the liquid recirculation rate. The final design shows a total equivalent sulfur recovery of 68.8% of the sulfur absorbed in the scrubber. To accomplish this it is necessary to air strip the weak SO_2 water solution which condenses out of the SO_2-rich stripper overhead vapors. Approximately 6% of the total sulfur equivalent is recovered in the air stripper.

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(2) "Investigation of the Steady State Characteristics of a Process for Obtaining 100% SO_2 from Ammonium Bisulfite", Gordeev, L. S. and Chertkov, B.A. (Vol. 7, No. 4) Inter. Chem. Eng.

The reaction of the sulfate, sulfite, bisulfite solution with $CaCO_3$ is assumed essentially 100% complete thus eliminating the need for a filtration step to recover ammonia values in the filtrate.

4. Process Design Appraisal

The ammonia scrubbing process is a relatively cheap and effective method for removing SO_2 from flue gas. It has a high absorption efficiency and requires fairly simple handling techniques in the scrubbing and regeneration steps. A disadvantage of this process which is common to all of the wet scrubbing processes is that the flue gas must be cooled and reheated.

As compared to limestone, ammonia is expensive and therefore must either be regenerated for recycle or become a constituent of a saleable product. In the process under evaluation all of the nitrogen in the scrubber effluent is regenerated either as $(NH_4)_2SO_3$ or NH_3 and recycled to the scrubber. Within the time and scope limitations of this study an attempt was made to select realistic operating conditions which would approach the optimum. Further study is indicated in the following areas to define the optimum process both with respect to cost and efficiency:

a. Establish the maximum S/C ratio attainable in the scrubber compatible with scrubber cost, ammonia losses, etc.

b. Establish the temperature-pressure conditions for carrying out the regeneration operation most efficiently.

c. Establish the optimum sulfate/sulfite-bisulfite ratio in the regenerator feed. This involves a comparison of the value of the recovered sulfur with the cost of higher recirculation rates.

d. Investigate the merits of direct steam injection versus indirect heating in the regeneration step.

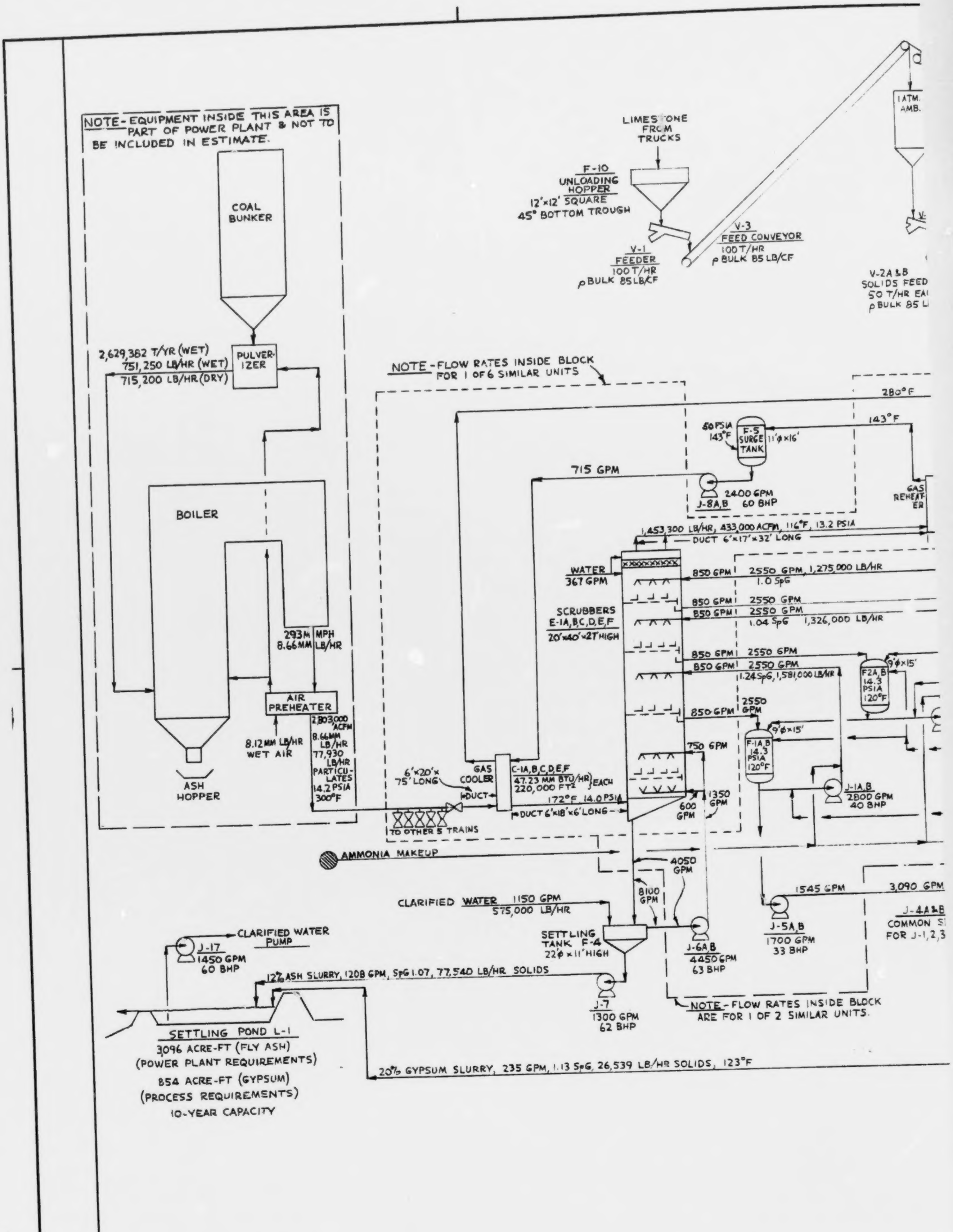
e. Reconcile, by laboratory tests, the vapor pressure calculations of Chertkov and Johnstone for the HN_3-SO_2-H_2O system.

f. Consider alternate methods of recovering the sulfur value from the sulfate rather than the proposed throwaway as $CaSO_4$.

Note: In addition to the references specifically cited in the text, the following two references also were used in this evaluation.

"Recovery of SO_2 from Waste Gases", Johnstone, H. F., IEC, Vol. 29 (1937).

"Recovery of SO_2 from Waste Gases", Johnstone, H. F., and Keyes, D. B., IEC, Vol. 27 (1935).


NOTE - EQUIPMENT INSIDE THIS AREA IS PART OF POWER PLANT & NOT TO BE INCLUDED IN ESTIMATE.
COAL BUNKER
PULVERIZER
2,629,382 T/YR (WET)
751,250 LB/HR (WET)
715,200 LB/HR (DRY)
BOILER
293 M MPH
8.66 MM LB/HR
AIR PREHEATER
8.12 MM LB/HR WET AIR
2,803,000 ACFM
8.66 MM LB/HR
77,930 LB/HR PARTICULATES
14.2 PSIA
300°F
ASH HOPPER
LIMESTONE FROM TRUCKS
F-10
UNLOADING HOPPER
12'×12' SQUARE
45° BOTTOM TROUGH
V-1
FEEDER
100 T/HR
ρ BULK 85 LB/CF
V-3
FEED CONVEYOR
100 T/HR
ρ BULK 85 LB/CF
1 ATM. AMB.
V-2A & B
SOLIDS FEED
50 T/HR EA
ρ BULK 85 L
NOTE - FLOW RATES INSIDE BLOCK FOR 1 OF 6 SIMILAR UNITS
280°F
143°F
50 PSIA
143°F
F-5 SURGE TANK
11'φ×16'
715 GPM
2400 GPM
J-8A,B
60 BHP
GAS REHEATER
1,453,300 LB/HR, 433,000 ACFM, 116°F, 13.2 PSIA
DUCT 6'×17'×32' LONG
WATER 367 GPM
SCRUBBERS E-1A,B,C,D,E,F
20'×40'×27' HIGH
850 GPM
2550 GPM, 1,275,000 LB/HR
1.0 SpG
850 GPM
2550 GPM
850 GPM
2550 GPM
1.04 SpG 1,326,000 LB/HR
850 GPM
2550 GPM
850 GPM
2550 GPM
1.24 SpG, 1,581,000 LB/HR
9'φ×15'
F2A,B
14.3 PSIA
120°F
850 GPM
2550 GPM
9'φ×15'
F-1A,B
14.3 PSIA
120°F
750 GPM
1350 GPM
600 GPM
J-1A,B
2800 GPM
40 BHP
6'×20'×75' LONG
DUCT
GAS COOLER
C-1A,B,C,D,E,F
47.23 MM BTU/HR
220,000 FT²
EACH
172°F, 14.0 PSIA
DUCT 6'×18'×6' LONG
TO OTHER 5 TRAINS
AMMONIA MAKEUP
4050 GPM
8100 GPM
1545 GPM
3,090 GPM
J-4A&B
COMMON S
FOR J-1,2,3
J-5A,B
1700 GPM
33 BHP
CLARIFIED WATER 1150 GPM
575,000 LB/HR
SETTLING TANK F-4
22'φ × 11' HIGH
J-6A,B
4450 GPM
63 BHP
NOTE - FLOW RATES INSIDE BLOCK ARE FOR 1 OF 2 SIMILAR UNITS.
J-17
CLARIFIED WATER PUMP
1450 GPM
60 BHP
12% ASH SLURRY, 1208 GPM, SpG 1.07, 77,540 LB/HR SOLIDS
J-7
1300 GPM
62 BHP
SETTLING POND L-1
3096 ACRE-FT (FLY ASH)
(POWER PLANT REQUIREMENTS)
854 ACRE-FT (GYPSUM)
(PROCESS REQUIREMENTS)
10-YEAR CAPACITY
20% GYPSUM SLURRY, 235 GPM, 1.13 SpG, 26,539 LB/HR SOLIDS, 123°F
15
H
G
F
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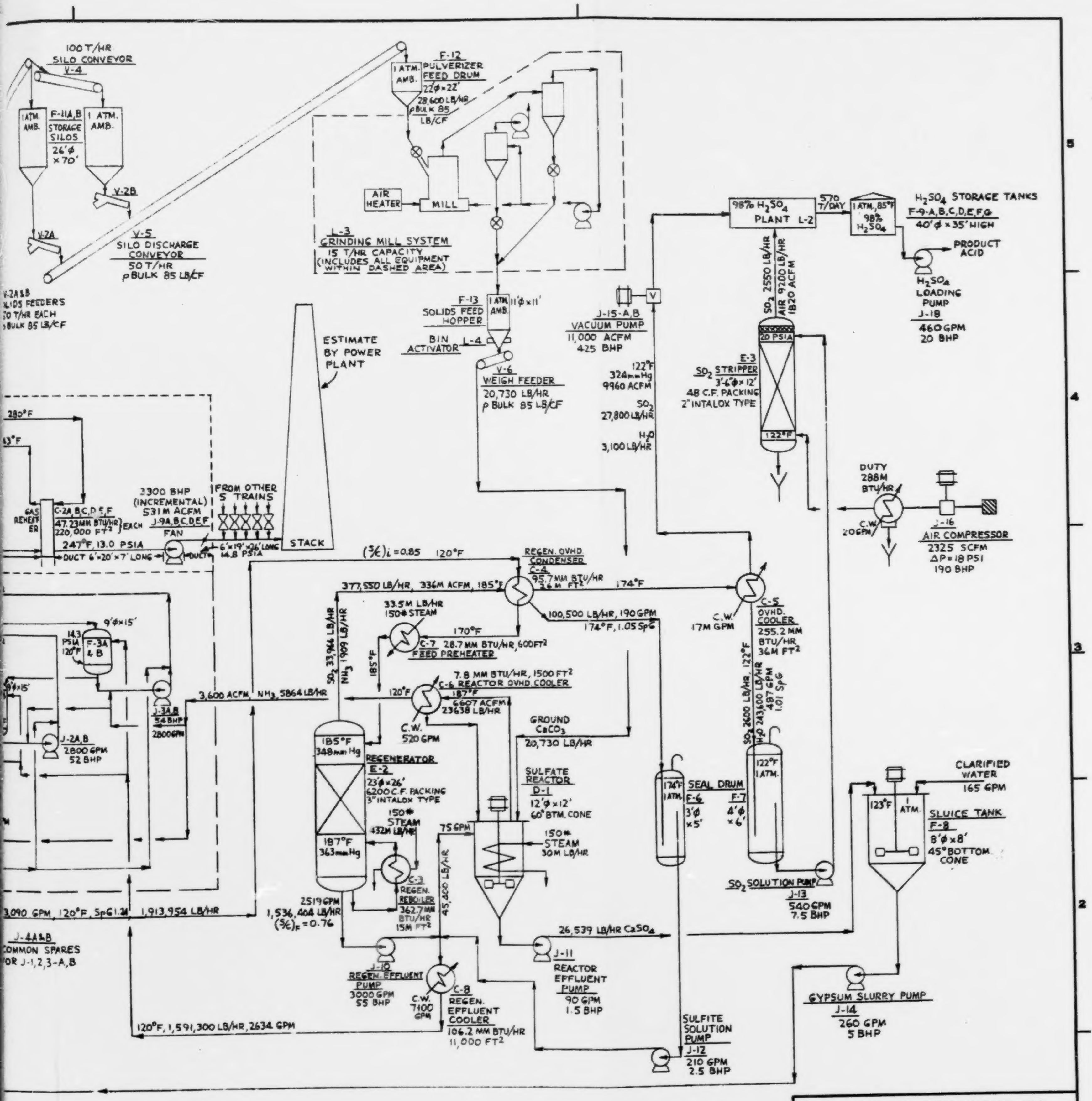
100 T/HR
SILO CONVEYOR
V-4
1 ATM. AMB.
F-11A,B
STORAGE SILOS
26'ϕ × 70'
1 ATM. AMB.
V-2B
V-2A
V-5
SILO DISCHARGE CONVEYOR
50 T/HR
ρ BULK 85 LB/CF
V-2A & B
SOLIDS FEEDERS
50 T/HR EACH
ρ BULK 85 LB/CF
1 ATM. AMB.
F-12
PULVERIZER FEED DRUM
22'ϕ × 22'
28,600 LB/HR
ρ BULK 85 LB/CF
AIR HEATER
MILL
L-3
GRINDING MILL SYSTEM
15 T/HR CAPACITY
(INCLUDES ALL EQUIPMENT WITHIN DASHED AREA)
F-13
SOLIDS FEED HOPPER
1 ATM. AMB.
11'ϕ × 11'
BIN ACTIVATOR L-4
V-6
WEIGH FEEDER
20,730 LB/HR
ρ BULK 85 LB/CF
ESTIMATE BY POWER PLANT
STACK
J-15-A,B
VACUUM PUMP
11,000 ACFM
425 BHP
V
122°F
324 mm Hg
9960 ACFM
SO2 27,800 LB/HR
H2O 3,100 LB/HR
98% H2SO4 PLANT L-2
570 T/DAY
1 ATM, 85°F
98% H2SO4
H2SO4 STORAGE TANKS
F-9-A,B,C,D,E,F,G
40'ϕ × 35' HIGH
PRODUCT ACID
H2SO4 LOADING PUMP
J-18
460 GPM
20 BHP
SO2 2550 LB/HR
AIR 9200 LB/HR
1820 ACFM
20 PSIA
E-3
SO2 STRIPPER
3'-6"ϕ × 12'
48 C.F. PACKING
2" INTALOX TYPE
122°F
DUTY
288M BTU/HR
C.W. 20 GPM
J-16
AIR COMPRESSOR
2325 SCFM
ΔP = 18 PSI
190 BHP
280°F
43°F
GAS REHEATER
C-2A,B,C,D,E,F
47.23 MM BTU/HR
220,000 FT2
EACH
3300 BHP (INCREMENTAL)
531M ACFM
J-9A,B,C,D,E,F
FAN
FROM OTHER 5 TRAINS
247°F, 13.0 PSIA
DUCT 6'×20'×7' LONG
DUCT
6'×19'×26' LONG
14.8 PSIA
(S/C)i = 0.85
120°F
REGEN. OVHD. CONDENSER
C-4
95.7 MM BTU/HR
26M FT2
377,550 LB/HR, 336M ACFM, 185°F
174°F
100,500 LB/HR, 190 GPM
174°F, 1.05 SpG
C.W. 17M GPM
C-5
OVHD. COOLER
255.2 MM BTU/HR
36M FT2
33.5M LB/HR
150# STEAM
170°F
C-7
28.7 MM BTU/HR, 600 FT2
FEED PREHEATER
185°F
SO2 33,966 LB/HR
NH3 1909 LB/HR
7.8 MM BTU/HR, 1500 FT2
C-6 REACTOR OVHD. COOLER
120°F
187°F
6607 ACFM
23638 LB/HR
C.W. 520 GPM
9'ϕ × 15'
14.3 PSIA
120°F
F-3A & B
9'ϕ × 15'
J-3A,B
54 BHP
2800 GPM
J-2A,B
2800 GPM
52 BHP
3,600 ACFM, NH3, 5864 LB/HR
GROUND CaCO3
20,730 LB/HR
185°F
348 mm Hg
REGENERATOR
E-2
23'ϕ × 26'
6200 C.F. PACKING
3" INTALOX TYPE
150# STEAM
432M LB/HR
187°F
363 mm Hg
C-3
REGEN. REBOILER
362.7 MM BTU/HR
15M FT2
SULFATE REACTOR
D-1
12'ϕ × 12'
60° BTM. CONE
75 GPM
150# STEAM
30M LB/HR
45,400 LB/HR
174°F
1 ATM.
SEAL DRUM
F-6
3'ϕ × 5'
F-7
4'ϕ × 6'
SO2 2600 LB/HR, 122°F
H2O 243,600 LB/HR
487 GPM
1.01 SpG
122°F
1 ATM.
SO2 SOLUTION PUMP
J-13
540 GPM
7.5 BHP
CLARIFIED WATER
165 GPM
123°F
1 ATM.
SLUICE TANK
F-8
8'ϕ × 8'
45° BOTTOM CONE
3,090 GPM, 120°F, SpG 1.24
1,913,954 LB/HR
2519 GPM
1,536,404 LB/HR
(S/C)F = 0.76
J-4A & B
COMMON SPARES FOR J-1,2,3-A,B
26,539 LB/HR CaSO4
J-10
REGEN. EFFLUENT PUMP
3000 GPM
55 BHP
C.W. 7100 GPM
C-8
REGEN. EFFLUENT COOLER
106.2 MM BTU/HR
11,000 FT2
J-11
REACTOR EFFLUENT PUMP
90 GPM
1.5 BHP
GYPSUM SLURRY PUMP
J-14
260 GPM
5 BHP
120°F, 1,591,300 LB/HR, 2634 GPM
SULFITE SOLUTION PUMP
J-12
210 GPM
2.5 BHP
5
4
3
2
1

THE M. W. KELLOGG CO.

PROCESS FOR REMOVAL OF SO_2 FROM POWER PLANT STACK GAS BY NH_3 SCRUBBING FOLLOWED BY REGENERATION OF $(NH_4)_2SO_3$ BY DECOMPOSITION OF NH_4HSO_3 WITH HEAT & STRIPPING OF GASEOUS PRODUCTS.
(ALTERNATE A)

ISSUE ① 4-15-71

NO.	DESCRIPTION	DATE	BY
4	GENERAL	5-19-71	W. B.
3	ADD LIMESTONE SYSTEM	4-21-71	W. B.
2	GENERAL	4-9-71	W. B.
1	GENERAL	3-29-71	W. B.

REVISIONS

SCALE: NONE
DRAWN: Beck
CHECKED:
APPROVED: C.J.R.
DATED:
ISSUED FOR FABRICATION
ISSUED FOR CONSTRUCTION

CLASS & ITEM	AREA	JOB NUMBER	DRAWING NUMBER
		4092-50	PD-113-D

D C DRAWING No. B A

187 A

B

AMMONIA SCRUBBING (ALTERNATE B)

(THERMAL DECOMPOSITION REGENERATION)

A. PROCESS

Sulfur dioxide removal from power plant stack gas by scrubbing with ammonia followed by acidification with NH_4HSO_4 and thermal decomposition of $(NH_4)_2SO_4$ for recovery of NH_3. Sulfur dioxide produced in the acidification step is used in the production of sulfuric acid.

1. Process Description (Refer to MWK Flow Sheet Dwg. No. PD-114-D)

   a. Sulfur Dioxide Removal From Flue Gas

Flue gas exits the air preheater at 300°F and is split into six parallel streams which flow thru identical scrubbing systems before being exhausted into a common stack. The gas is first cooled to 172°F in gas cooler C-1. The cooled gas containing 4.9 gr of solid particulates/SCF is scrubbed with water on the bottom tray of a four-stage scrubbing tower E-1. 99.5 wt % of the solids-are removed and discharged to settling tank F-4 common to the six scrubbers. The solids are settled out and diluted with water to a 12 wt % ash slurry which is pumped to a settling pond. The solids free gas flows countercurrent to the wash solution containing NH_3, SO_2, $(NH_4)_2SO_3$, NH_4HSO_3 and $(NH_4)_2SO_4$. Three stages are required to remove 90 wt % of the SO_2 by reaction with NH_3 and $(NH_4)_2SO_3$. The proposed scrubbers are countercurrent seive tray type Impinjet gas scrubbers manufactured by the W. W. Sly Mfg. Co.

Six scrubbers are required to handle the flue gas from a 1000 MW plant since the largest scrubber available is 20' wide x 40' long. The total sidestream drawoff from each of the three wash trays is segregated flowing respectively to the recirculation surge tanks F-1, 2, 3. Each tank is common to three scrubbers resulting in two recirculation systems each of which feeds three scrubbers via pumps J-1, 2, 3. Regenerated NH_3 is added to each recirculation stream and the liquid composition on the trays is regulated by drawing off a slipstream from each drum flowing stepwise from F-3 to F-2 to F-1. The scrubber effluent product is withdrawn from drums F-1A, B and pumped to acidifier/stripper E-2. The scrubber effluent consists of 48.5 wt % salt solution containing a mixture of SO_2, NH_3 and ammonium sulfite, bisulfite and sulfate. The flue gas is cooled adiabatically in the scrubber by the evaporation of water and leaves the scrubber saturated at 116°F. Makeup water is injected into the scrubber above the top tray and liquid entrainment is removed by a fixed blade impingement baffle located in the top of the scrubber. The gas is reheated to 247°F in gas reheater C-2 to ensure adequate dispersion of the gas leaving the stack. Flow thru the scrubbers is maintained by exhaust fan J-9 located downstream of gas reheater C-2. The six fans exhaust to a common stack and maintain the entire system under slight negative pressure. A pumparound system utilizing surge tank F-5 and pump J-8 circulates tempered water thru gas cooler C-1 and gas reheater C-2 in series transferring heat from C-1 to C-2.

b. Regeneration of Scrubber Effluent for Recovery of Ammonia and Sulfur Dioxide

The combined effluent from the six scrubbers is pumped from tanks F-1A, B and heated to 158°F in preheater E-3. The scrubber effluent is then combined, by line mixing, with the molten salt slurry from the electric furnaces B-1A, B, C, D, E and discharged into the top section of the acidifier/stripper column E-2. The acidifier/stripper is a packed column with top outlet operating conditions of 158°F and 378 mm Hg absolute pressure. Thermosiphon reboiler E-4 heated by the overhead vapors from evaporator/crystallizer E-3 provides vapor boilup. The acidifier/stripper column is primarily a mixing and heating device to enable the following reactions to rapidly proceed to completion;

1. $NH_4HSO_3(AQ\ SOLN)+NH_4HSO_4(AQ\ SOLN)\xrightarrow{HEAT}(NH_4)_2SO_4(AQ\ SOLN)+SO_2\uparrow+H_2O(l)$

2. $(NH_4)_2SO_3(AQ)+2NH_4HSO_4(AQ)\xrightarrow{HEAT}2(NH_4)_2SO_4(AQ)+SO_2\uparrow+H_2O(l)$

The acidifier/stripper effluent consisting of $(NH_4)_2SO_4$ and excess NH_4HSO_4 in aqueous solution containing a small amount of dissolved SO_2 is pumped thru preheater C-7 where it is first heated to 266°F and then discharged into evaporator/crystallizer E-3. The overhead vapor from E-2 is cooled with water to 122°F in C-6 where most of the water condenses out and drains to condensate drum F-6. The remaining SO_2-rich vapor is pumped via vacuum pump J-17 to a sulfuric acid plant L-2. Total sulfur recovery is 18,473 lb/hr representing 83.7% of the sulfur removed from the flue gas. The acid plant produces 692 tons/CD of 98% acid. The evaporator/crystallizer E-3 is heated by forced circulation reboiler C-10 which vaporizes 96% of the water of solution along with the dissolved SO_2. The vapor from E-2 flows in series thru exchangers C-3, C-4 and C-5 where it is condensed and cooled. The combined condensate from exchangers C-3, C-4, C-5 and C-6 is collected in condensate drum F-6 from which it is pumped to the sulfate reactor D-1 where the 579 lb/hr of dissolved SO_2 is neutralized with $CaCO_3$.

The wet ammonium salts which crystallize out in E-2 are conveyed to the electric furnaces B-1A, B, C, D, E. The following decomposition reaction takes place in the furnaces;

$$(NH_4)_2SO_4(s) \xrightarrow[700^\circ F]{HEAT} NH_4HSO_4(l) + NH_3\uparrow$$

Higher temperature will promote undesirable secondary decomposition reactions producing unusable ammonium salts. By maintaining the temperature at 700°F and by injecting 700°F superheated steam throughout the furnace melt these secondary reactions are minimized. Approximately 80% of the $(NH_4)_2SO_4$ in the feed is converted to NH_4HSO_4. The furnace effluent stream containing 83 mole % NH_4HSO_4 and 17 mole % $(NH_4)_2SO_4$ is recycled to the acidifier stripper after first being cooled to 350°F in exchanger C-7. A slipstream comprising 9 wt % of the total furnace effluent is pumped to the sulfate reactor D-1 after first being mixed with the SO_2/H_2O solution from condensate drum F-6 and cooled to 175°F in exchanger C-9. The ammonium salts contained in this stream are reacted with $CaCO_3$ for removal of the net sulfate make in the scrubbers. The following reactions take place in the sulfate reactor;

1. $(NH_4)_2SO_4(AQ\ SOLN)+CaCO_3(s)\xrightarrow{+HEAT}CaSO_4\downarrow+2NH_3\uparrow+CO_2\uparrow+H_2O(l)$

2. $NH_4HSO_4(AQ\ SOLN)+CaCO_3(s)\xrightarrow{-HEAT}CaSO_4\downarrow+NH_3\uparrow+CO_2\uparrow+H_2O(l)$

3. $SO_2+CaCO_3+2H_2O\rightarrow CaSO_3\cdot 2H_2O\downarrow+CO_2\uparrow$

The net overall heat effect in the sulfate reactor is exothermic requiring the use of water cooled internal coils for heat removal. The resulting insoluble $CaSO_4$ is settled out and pumped to the settling pond. The vapor from the reactor containing NH_3, CO_2 and H_2O is combined with the vapor from the electric furnaces containing NH_3 and H_2O and is then cooled to 120°F in exchanger C-8 where most of the water condenses out and is sewered. The noncondensible NH_3 and CO_2 vapor is recycled back to the scrubbers.

2. Process Design Basis

Basic process design criteria common to all of the SO_2 removal processes being evaluated are not included in the following list.

Overall Plant Capacity Factor, % of Nameplate Rating

1st to 10th year	80%
11th to 15th year	57%
16th to 20th year	40%
21st to 35th year	17%
Average Capacity Factor	43%

a. Ammonia Scrubbers E-1A, B, C, D, E, F

The following data pertaining to the scrubbers selected as being most suitable for this service was obtained from the W. Sly Mfg. Co. bulletin and is applicable to the cross flow sieve tray impinjet type gas scrubber.

Quantity (6) Six

Dimensions 20' x 40' (rect.) x 27' high

Design Gas Velocity, Nor. 420 fpm, max. 500 fpm, actual 461 fpm

Fly Ash Dust Removal 99.5% (total fly ash from boiler)
Water recirculation to bottom scrubber stage for dust removal
Combined plate and spray water, 3 gpm/1000 ACFM gas

b. Scrubber Operating Conditions

Gas inlet temp., 172°F
Gas outlet temp., 116°F
Effluent temp., 120°F
Effluent salt concentration, 48.5 wt %
Effluent S:NH_3 mole ratio, S/C = 0.85
Salt solution recirculation rate, 1.06 gal/min-ft^2
Fly ash slurry concentration to settling pond, 12 wt % solids

c. Acidifier/Stripper E-2

Liquid inlet temp., 215°F
Liquid outlet temp., 160°F
Tower top abs. pres., 378 mm Hg
Tower bottom abs. pres., 398 mm Hg
Feed composition, $(S/C)_i = 0.85$
NH_4HSO_4 in feed = 1.25 x stoichiometric requirements
Theoretical stages, 4
Liquid flow rate L, 1.17 lb/sec-ft^2
Gas flow rate G, 0.423 lb/sec-ft^2
Packing type, 3" Intalox saddles

d. Sulfate Reactor, D-1

Operating temp., 185°F
Operating Pres., 18 psia
Retention time, 30 minutes
$CaCO_3$ in feed, 1.25 x stoichiometric requirements

e. Evaporator/Crystallizer, E-3

Oper. Temp., 212°F
Oper. Pres., 930 mm Hg
Retention time, 22 minutes
Reboiler recirculation rate, 415 gpm
% of water vaporized, 96

f. Electric Furnace, B-1A, B, C, E, E

Operating temp., 700°F

Operating Pres., 3 psig

Feed temp., 212°F

$(NH_4)_2SO_4$ conversion, 80%

Electrical Power Consumption, 350 KWH/ton of $(NH_4)_2SO_4$ in feed

Steam injection rate, 0.2 lb stream/lb $(NH_4)_2SO_4$ in feed (700°F superheated)

Design capacity of unit, 5000 KW

Number units required, (5) five

Total working capacity, 22400 KW

Power supply characteristics, 3 phase, variable voltage 120 to 164 V

Furnace dimensions, 20' Dia. x 10' Deep

g. Settling Pond L-1

Basis: 10 years combined production of gypsum and recovered fly ash.

Fly ash, 3096 acre-ft

Gypsum, 576 acre-ft

3. Process Design Rationale

A scrubber effluent with a high S/C ratio is beneficial to the acidification/stripping process since a high NH_4HSO_3 content would require fewer moles of NH_4HSO_4 for acidification thereby reducing the duty of the thermal decomposition furnaces. Therefore the scrubbing operation as used for alternate A case (regeneration by steam stripping) which had a scrubber effluent with an S/C ratio of 0.85 is used without change for the alternate B design. The operating conditions for the acidification/stripping column were chosen to give a favorable SO_2/H_2O ratio in the overhead vapor stream and to permit utilization of a part of the heat available in the evaporator/crystallizer overhead vapor stream for preheating the feed stream. The regenerated molten NH_4HSO_4 stream and the scrubber effluent are line mixed prior to injection into the acidifier/stripper to facilitate heat transfer and promote the acidification reactions. This will more closely simulate the basic design assumption that the mixture of SO_2 and H_2O vapor is in equilibrium with an aqueous solution of SO_2 and sulfates. The NH_4HSO_4 feed rate to the acidifier/stripper is set at 1.25 times the stoichiometric requirements to ensure complete reaction of the sulfites.

The performance data pertaining to the electric furnaces used for decomposition of the $(NH_4)_2SO_4$ were obtained from the report(1) covering an experimental plant for producing alumina. The performance of these furnaces which is critical to this process seems to be well enough established to remove any doubts as to the feasibility of the process. The important operating parameters covered in the report are 80% conversion of $(NH_4)_2SO_4$ to NH_4HSO_4 at 700°F with minumum secondary reactions provided superheated steam is injected into the melt to retard such reactions and an actual power consumption of 350 KWH per ton of $(NH_4)_2SO_4$ charged to the furnace. The combined condensate from the acidifier/stripper overhead and evaporator/crystallizer overhead streams contains such a relatively small amount of SO_2 (579 lb/hr, 0.8 wt %) that it does not warrant further treatment for recovery of the SO_2 value. Therefore this stream is combined with the slipstream from the electric furnace effluent and reacted with $CaCO_3$ in the sulfate reactor. $CaCO_3$ feed to the sulfate reactor is 1.25 x stoichiometric to ensure complete recovery of the NH_3 from the ammonium salts.

4. Process Design Appraisal

The ammonia scrubbing process is a relatively cheap and effective method for removing SO_2 from flue gas. It has a high absorption efficiency and requires fairly simple handling techniques in the scrubbing and regeneration steps. A disadvantage of this process which is common to all of the wet scrubbing processes is that the flue gas must be cooled and reheated.

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(1) Engineer-Contractor's Report on Alumina-From-Clay, Experimental Plant (Plancor 1865) at Salem, Oregon. Chemical Construction Corp., N.Y., N.Y.

As compared to limestone, ammonia is expensive and therefore must either be regenerated for recycle or become a constituent of a saleable product. In the process under evaluation all of the nitrogen in the scrubber effluent is regenerated as NH_3 and recycled to the scrubber. Within the time and scope limitations of this study an attempt was made to select realistic operating conditions which would approach the optimum. Further study is indicated in the following areas to define the optimum process both with respect to cost and efficiency:

a. $\underline{NH_3\ \text{Scrubber}}$, establish the maximum S/C ratio attainable in the scrubber compatible with scrubber cost, ammonia loses, etc.

b. Acidifier/Stripper, establish the optimum operating temperature and pressure. Determine the best method of handling the molten effluent from the electric furnaces particularly with respect to premixing, cooling and injection into the acidifier/stripper. Determine the most suitable vessel internal configuration to obtain adequate mixing for rapid and complete sulfite reaction. Determine actual composition of overhead vapor in equilibrium with non-idealized liquid in vessel. Determine the minimum excess NH_4HSO_4 required for complete reaction of sulfites.

c. Electric Furnace, establish the optimum operating temperature, and steam injection rate compatible with percent conversion, extent of secondary reactions and power input. Determine required residence time for equipment sizing.

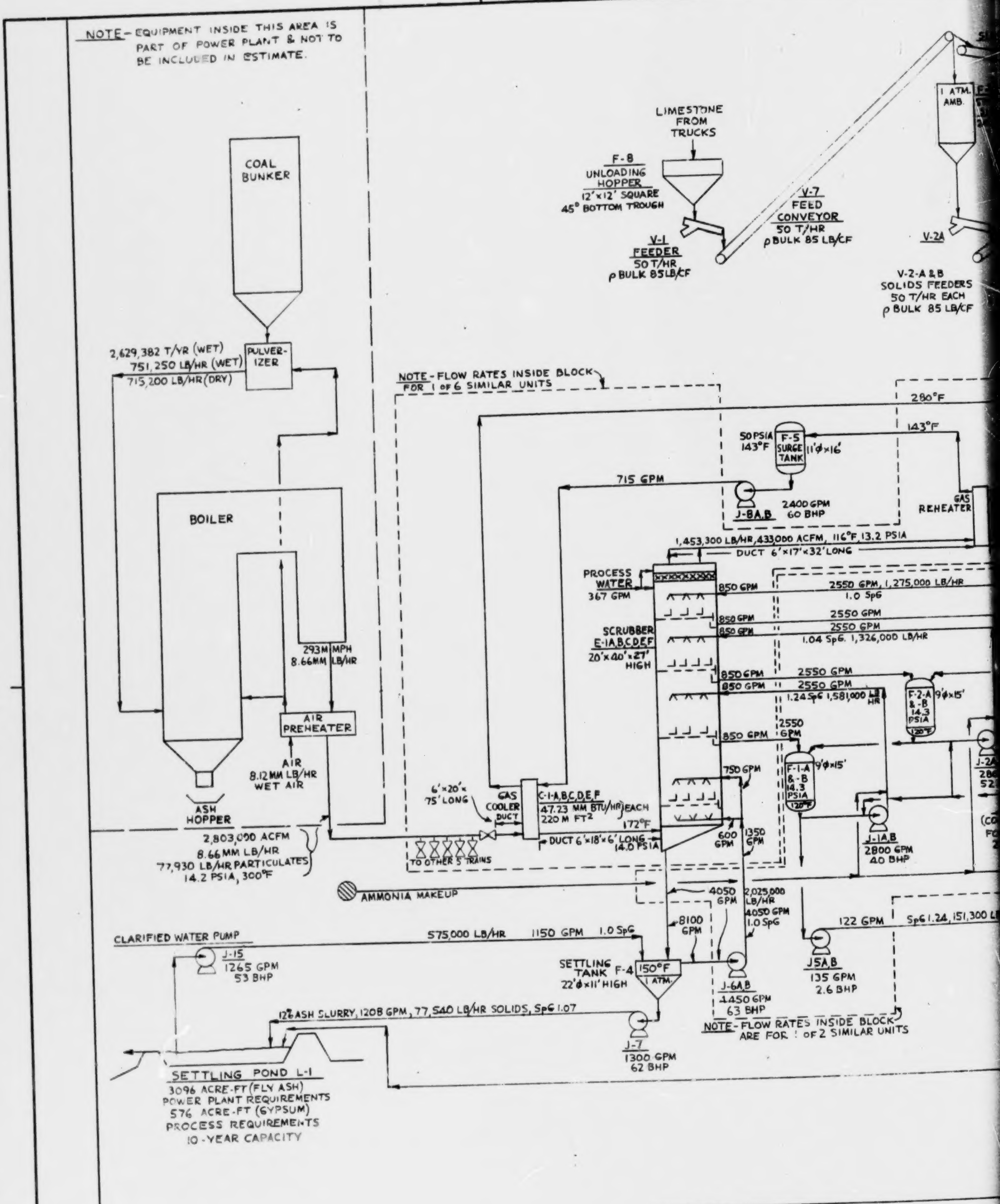
d. Sulfate Reactor/Settler, establish optimum reaction temperature, residence time and excess $CaCO_3$ requirements for reaction to go to completion. Determine the most satisfactory slurry concentration with respect to handling characteristics.

e. $\underline{NH_3\ \text{Losses}}$; determine overall system NH_3 losses.

Additional References

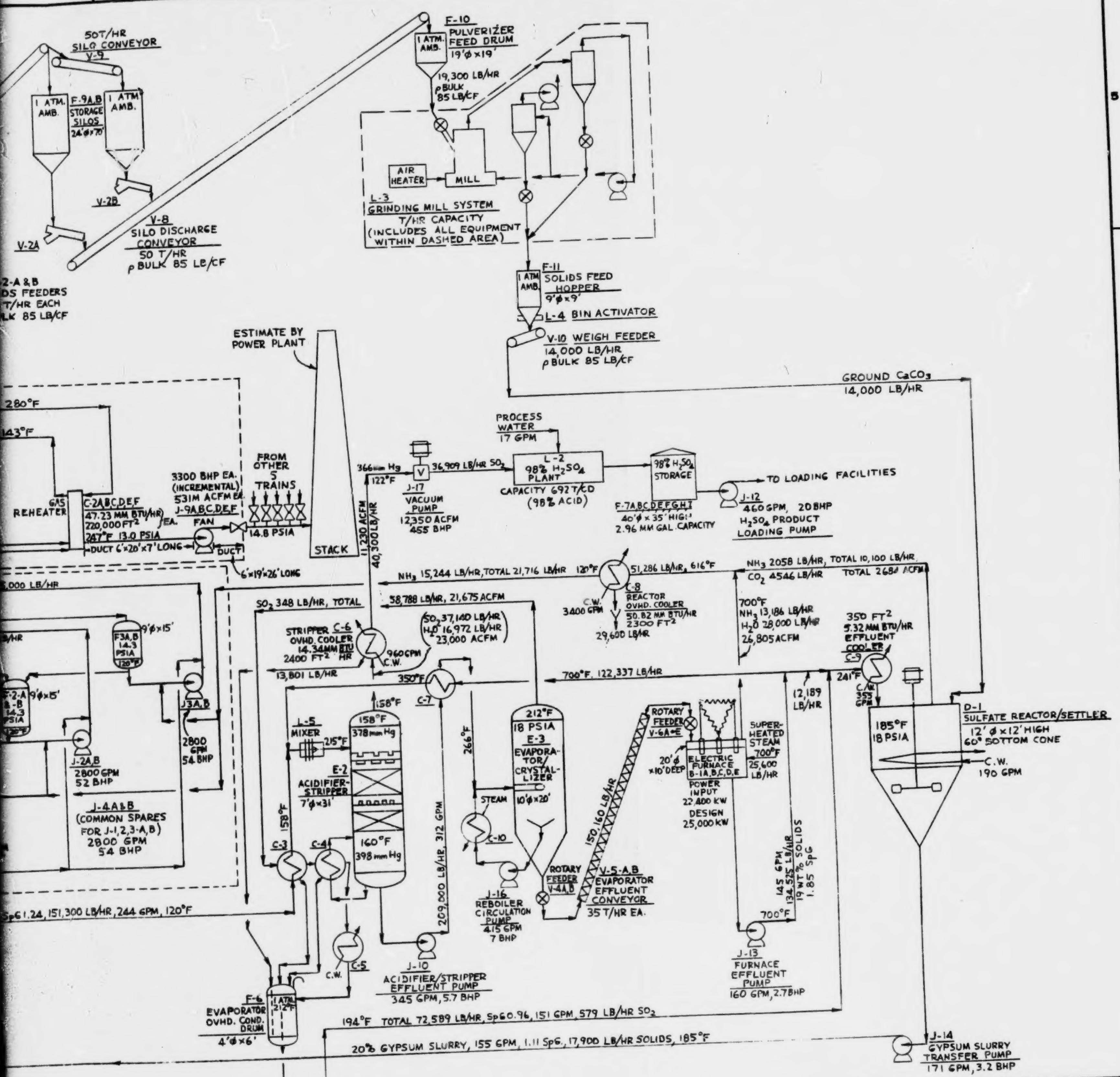
1. U.S. Patent 2,405,717, Recovery of Acidic Gases, A. W. Hixson and R. Miller (1946).

2. "Sulfur Dioxide Removal From Power Plant Stack Gas, Ammonia Scrubbing", Conceptual Design and Cost Series Study No. 3, 1970, Contract No. TV 29233A.


NOTE - EQUIPMENT INSIDE THIS AREA IS PART OF POWER PLANT & NOT TO BE INCLUDED IN ESTIMATE.
COAL BUNKER
2,629,382 T/YR (WET)
751,250 LB/HR (WET)
715,200 LB/HR (DRY)
PULVERIZER
BOILER
293M MPH
8.66MM LB/HR
AIR PREHEATER
AIR
8.12MM LB/HR
WET AIR
ASH HOPPER
2,803,000 ACFM
8.66MM LB/HR
77,930 LB/HR PARTICULATES
14.2 PSIA, 300°F
LIMESTONE FROM TRUCKS
F-8
UNLOADING HOPPER
12'×12' SQUARE
45° BOTTOM TROUGH
V-1
FEEDER
50 T/HR
ρ BULK 85 LB/CF
V-7
FEED CONVEYOR
50 T/HR
ρ BULK 85 LB/CF
1 ATM.
AMB.
V-2A
V-2-A & B
SOLIDS FEEDERS
50 T/HR EACH
ρ BULK 85 LB/CF
NOTE - FLOW RATES INSIDE BLOCK FOR 1 OF 6 SIMILAR UNITS
50 PSIA
143°F
F-5
SURGE TANK
11'ϕ×16'
715 GPM
J-8A,B
2400 GPM
60 BHP
280°F
143°F
GAS REHEATER
1,453,300 LB/HR, 433,000 ACFM, 116°F, 13.2 PSIA
DUCT 6'×17'×32' LONG
PROCESS WATER
367 GPM
850 GPM
2550 GPM, 1,275,000 LB/HR
1.0 SpG
850 GPM
2550 GPM
850 GPM
2550 GPM
1.04 SpG. 1,326,000 LB/HR
SCRUBBER
E-1A,B,C,D,E,F
20'×40'×27' HIGH
850 GPM
2550 GPM
850 GPM
2550 GPM
1.24 SpG 1,581,000 LB/HR
F-2-A & -B
14.3 PSIA
120°F
9'ϕ×15'
850 GPM
2550 GPM
F-1-A & -B
14.3 PSIA
120°F
9'ϕ×15'
J-1A,B
2800 GPM
40 BHP
750 GPM
6'×20'×75' LONG
GAS COOLER DUCT
C-1-A,B,C,D,E,F
47.23 MM BTU/HR
220 M FT²
EACH
172°F
DUCT 6'×18'×6' LONG
14.0 PSIA
600 GPM
1350 GPM
TO OTHER 5 TRAINS
AMMONIA MAKEUP
4050 GPM
2,025,000 LB/HR
4050 GPM
1.0 SpG
8100 GPM
122 GPM
SpG 1.24, 151,300 L
J5A,B
135 GPM
2.6 BHP
CLARIFIED WATER PUMP
J-15
1265 GPM
53 BHP
575,000 LB/HR
1150 GPM
1.0 SpG
SETTLING TANK F-4
22'ϕ×11' HIGH
150°F
1 ATM.
J-6A,B
4450 GPM
63 BHP
NOTE - FLOW RATES INSIDE BLOCK ARE FOR 1 OF 2 SIMILAR UNITS
12% ASH SLURRY, 1208 GPM, 77,540 LB/HR SOLIDS, SpG 1.07
J-7
1300 GPM
62 BHP
SETTLING POND L-1
3096 ACRE-FT (FLY ASH)
POWER PLANT REQUIREMENTS
576 ACRE-FT (GYPSUM)
PROCESS REQUIREMENTS
10-YEAR CAPACITY
H
G
F
E

CONDENSERS, HEATERS, & HEAT EXCHANGERS

NO.	SERVICE	DUTY BTU/HR	WATER GPM	STEAM LB/HR	SUR SQ.
C-3	STRIPPER FEED PREHEATER	5.75 MM	—	—	7
C-4	ACIDIFIER/STRIPPER REBOILER	7.86 MM	—	—	15
C-5	EVAP. OVHD. CONDENSER	43.955 MM	2930	—	21
C-7	EVAP./CRYS. FEED PREHEATER	21.19 MM	—	—	15
C-10	EVAPORATOR/CRYSTALLIZER REBOILER	43.97 MM	—	51,300	15


50T/HR
SILO CONVEYOR
V-9
1 ATM. AMB.
F-9A,B STORAGE SILOS 24'φ×70'
1 ATM. AMB.
V-2B
V-2A
V-8
SILO DISCHARGE CONVEYOR
50 T/HR
ρBULK 85 LB/CF
-2-A & B
DS FEEDERS
T/HR EACH
LK 85 LB/CF
F-10
PULVERIZER FEED DRUM
19'φ×19'
1 ATM. AMB.
19,300 LB/HR
ρBULK 85 LB/CF
AIR HEATER
MILL
L-3
GRINDING MILL SYSTEM
T/HR CAPACITY
(INCLUDES ALL EQUIPMENT WITHIN DASHED AREA)
F-11
1 ATM AMB.
SOLIDS FEED HOPPER
9'φ×9'
L-4 BIN ACTIVATOR
V-10 WEIGH FEEDER
14,000 LB/HR
ρBULK 85 LB/CF
GROUND CaCO3
14,000 LB/HR
ESTIMATE BY POWER PLANT
STACK
280°F
143°F
GAS REHEATER
C-2A,B,C,D,E,F
47.23 MM BTU/HR
220,000 FT2 EA.
247°F 13.0 PSIA
DUCT 6'×20'×7' LONG
3300 BHP EA. (INCREMENTAL)
531M ACFM EA.
J-9A,B,C,D,E,F
FAN
DUCT
6'×19'×26' LONG
FROM OTHER 5 TRAINS
14.8 PSIA
11,230 ACFM
40,300 LB/HR
366mm Hg
122°F
V
J-17
VACUUM PUMP
12,350 ACFM
455 BHP
36,909 LB/HR SO2
PROCESS WATER
17 GPM
L-2
98% H2SO4 PLANT
CAPACITY 692 T/CD (98% ACID)
98% H2SO4 STORAGE
F-7A,B,C,D,E,F,G,H,I
40'φ×35' HIGH
2.96 MM GAL. CAPACITY
J-12
460 GPM, 20 BHP
H2SO4 PRODUCT LOADING PUMP
TO LOADING FACILITIES
,000 LB/HR
NH3 15,244 LB/HR, TOTAL 21,716 LB/HR
120°F
51,286 LB/HR, 616°F
C.W. 3400 GPM
C-8
REACTOR OVHD. COOLER
50.82 MM BTU/HR
2300 FT2
29,600 LB/HR
NH3 2058 LB/HR, TOTAL 10,100 LB/HR
CO2 4546 LB/HR TOTAL 2684 ACFM
700°F
NH3 13,186 LB/HR
H2O 28,000 LB/HR
26,805 ACFM
SO2 348 LB/HR, TOTAL
58,788 LB/HR, 21,675 ACFM
(SO2 37,140 LB/HR
H2O 16,972 LB/HR
23,000 ACFM)
STRIPPER OVHD. COOLER C-6
14.34MM BTU/HR
2400 FT2
960 GPM
C.W.
13,801 LB/HR
F3A,B 14.3 PSIA 120°F
9'φ×15'
J-3A,B
F-2-A,B
14.3 PSIA
9'φ×15'
J-2A,B
2800 GPM
52 BHP
2800 GPM
54 BHP
J-4A&B
(COMMON SPARES FOR J-1,2,3-A,B)
2800 GPM
54 BHP
350°F
C-7
158°F
L-5
MIXER
215°F
158°F
378mm Hg
E-2
ACIDIFIER-STRIPPER
7'φ×31'
160°F
398mm Hg
158°F
C-3
C-4
C-5
C.W.
209,000 LB/HR, 312 GPM
J-10
ACIDIFIER/STRIPPER EFFLUENT PUMP
345 GPM, 5.7 BHP
700°F, 122,337 LB/HR
266°F
212°F
18 PSIA
E-3
EVAPORATOR/CRYSTALLIZER
10'φ×20'
STEAM
C-10
J-16
REBOILER CIRCULATION PUMP
415 GPM
7 BHP
ROTARY FEEDER V-4A,B
V-5-A,B
EVAPORATOR EFFLUENT CONVEYOR
35 T/HR EA.
150,160 LB/HR
ROTARY FEEDER V-6A-E
20'φ ×10' DEEP
ELECTRIC FURNACE B-1A,B,C,D,E
POWER INPUT 22,400 KW
DESIGN 25,000 KW
SUPER-HEATED STEAM
700°F
25,600 LB/HR
12,189 LB/HR
145 GPM
134,525 LB/HR
19 WT% SOLIDS
1.85 SpG
700°F
J-13
FURNACE EFFLUENT PUMP
160 GPM, 2.7 BHP
350 FT2
5.32 MM BTU/HR
EFFLUENT COOLER
C-9
241°F
C.W. 355 GPM
D-1
SULFATE REACTOR/SETTLER
12'φ×12' HIGH
60° BOTTOM CONE
185°F
18 PSIA
C.W.
190 GPM
SpG 1.24, 151,300 LB/HR, 244 GPM, 120°F
F-6
1 ATM 212°F
EVAPORATOR OVHD. COND. DRUM
4'φ×6'
194°F TOTAL 72,589 LB/HR, SpG 0.96, 151 GPM, 579 LB/HR SO2
20% GYPSUM SLURRY, 155 GPM, 1.11 SpG., 17,900 LB/HR SOLIDS, 185°F
J-14
GYPSUM SLURRY TRANSFER PUMP
171 GPM, 3.2 BHP
J-11
EVAPORATOR CONDENSATE PUMP
165 GPM, 38HP

S		
TER PM	STEAM LB/HR	SURFACE SQ. FT.
—	—	700
—	—	1500
930	—	2100
—	—	1500
—	51,300	1500

196A

THE M. W. KELLOGG CO.

PROCESS FOR REMOVAL OF SO_2 FROM POWER
PLANT STACK GAS BY NH_3 SCRUBBING
FOLLOWED BY REGENERATION OF AMMONIA BY
ACIDIFICATION & THERMAL DECOMPOSITION
(ALTERNATE B)

SCALE: NONE
DRAWN: Beck
CHECKED:
APPROVED: C.J.R.
DATED: 3-19-71
ISSUED FOR FABRICATION
ISSUED FOR CONSTRUCTION

NO.	DESCRIPTION	DATE	BY	CHECKED
2	GENERAL	5-19-71		
1	GENERAL	4-30-71	W.B.	

REVISIONS

CLASS & ITEM	AREA	JOB NUMBER	DRAWING NUMBER
		4092-50	PD-114-D

D C DRAWING NO. B A

5 4 3 2 1

TYCO PROCESS

A. PROCESS

1. Process Description (See MWK Dwg No. PD-116-D)

The process described below is based on the TYCO Modified Chamber Process for the removal of SO_2 and NO_x from electric power plant flue gases (1). The sulfur and nitrogen oxide pollutants are removed as sulfuric and nitric acids. The flue gas to be treated is based on the burning of 3.5 wt % sulfur coal in a 1000 megawatt coal-fired power plant. Sulfur levels in the flue gas are 0.261 mole % SO_2 and 0.005 mole % SO_3; NO_x is assumed to be 500 ppm, by volume. Removals of 90% SO_x and 80% NO_x are assumed.

Flue gas (95% fly ash-free after electrostatic precipitation) is split into four parallel trains, and the pressure increased via flue gas fans, J-1a-d, from 14.05 psia to 16.05 psia to supply the necessary head to move the gas through the downstream equipment. The flue gas is then injected with an NO_2-rich (10 mole %) gas recycled from the downstream catalytic stripper, E-2. Enough NO_2 is injected into the flue gas such that about 90% of the SO_2 is oxidized to SO_3 in SO_2 oxidizer reactor, D-1, with a resulting NO_2 to NO ratio of 1 to 1. The reaction is:

$$SO_2 + NO_2 = SO_3 + NO \qquad (1)$$

The SO_3 combines with water vapor to form H_2SO_4. Any oxidation of NO to NO_2 is assumed negligible - a reasonable assumption considering the 300°F temperature and low oxygen partial pressure.

The effluent from D-1, at 328°F, is sent to N_2O_3 scrubber, E-1, where NO_x is absorbed as N_2O_3 and the H_2SO_4 recovered via condensation of SO_3 and H_2O. Over 98% absorption of N_2O_3 is required in order to achieve the overall 80% NO_x recovery; this is owing to the fact that 11-fold as much NO_x is recycled as is present in the original flue gas. The NO_2-NO is absorbed by contacting with 267°F, 80% H_2SO_4 in the packed scrubber, E-1. The absorption-reaction produces 0.3 wt % nitrosylsulfuric acid dissolved in 80 wt % H_2SO_4 according to the following reaction:

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(1) Gruber, A., and Walitt, A., "Oxidation of SO_2" - Final Report, Contract CPA 70-59 for NAPCA, 1970.

$$NO + NO_2 + 2H_2SO_4 = 2HNSO_5 + H_2O \qquad (2)$$

The scrubbed gas passes through a high velocity mist eliminator, L-2, to recover entrained sulfuric acid mist before the flue gas enters the stack. The scrubber overhead temperature is set such that the partial pressure of water vapor over 80% H_2SO_4 will result in a scrubbing operation in which there will be no unnecessary absorption or stripping of water. The partial pressure of H_2SO_4 over 80% acid (1) at 267°F yields a 66 ppm H_2SO_4 concentration in the flue gas - corresponding to a loss of about one ton per hour.

The scrubber, E-1, will also pick up the fly ash which has not been removed in the precipitator. According to experimental work performed by TVA (2) about 20% of the fly ash constituents are soluble in hot, 80% sulfuric acid. (The saturation point is not reported.) The undissolved ash has to be removed from the circulating acid before it is sent downstream to the catalytic stripper. The process flow-sheet shows 272°F bottoms liquid from E-1 pumped by J-2 to an undefined "black-box", L-1, which contains the ash removal facilities. A 50% by weight ash/acid mixture is shown leaving L-1 and is neutralized by addition of sluice water and limestone. About 3100 lb/hr of acid is lost to neutralization with the ash. The undissolved ash amounts to less than .005 wt % in the liquid acid. A more detailed study of solids/liquid separation at such low solids levels is needed before this section can be specified. The dissolved ash will build up until the purge rate of dissolved ash in the sulfuric acid product equals the input ash rate with the flue gas. The build-up is to about 0.9 wt-% dissolved ash in the circulating acid.

The solid-free acid leaves the ash removal facilities and flows to F-4 surge tank. This sulfuric-nitrosylsulfuric mixture is then pumped via J-3 to the top of the oxidizing stripper, E-2.

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(1) Gmitro, J.I., and Vermeulen, T., "Vapor-Liquid Equilibria for Aqueous Sulfuric Acid", UCRL-10886, Univ. Calif., Berkeley, June 24, 1963.

(2) TVA, "Sulfur Oxide Removal From Power Plant Stack Gases - TYCO Process", Preliminary Conceptual Design and Cost Study (Draft) Contract TV-29233A, 1/18/71.

The liquid flows over a bed of granular activated carbon countercurrent to a stream of air. The TYCO concept indicates that this activated carbon will act as a catalyst to promote the oxidation of the dissolved $HNSO_5$ to gaseous NO_2 and H_2SO_4:

$$4HNSO_5 + 2H_2O + O_2 \underset{CAT}{=} 4H_2SO_4 + 4NO_2 \tag{3}$$

An extremely high stripping efficiency of 99% and an off-gas from the stripper of about 10% NO_2 are required. The high efficiency gives the required NO^+-free scrubbing acid to be recycled to E-1, and an NO^+-free H_2SO_4 product. The 10% NO_2 level allows for the economic production of HNO_3 by cold absorption of NO_2 into water.

The necessary air for the reacting/stripping operation is supplied by air blower J-5, operating at a ΔP of 30" w.g. A slip-stream of the 80% H_2SO_4 from E-2 is cooled to 100°F in product cooler C-2 and sent to storage. Net product acid amounts to 80,920 lb/hr of 80% acid. The remaining hot acid from E-2 is pumped by J-4 to recycle acid cooler, C-1, and then scrubber E-1 to complete the acid circulating loop. Cooler C-1 cools the acid from 272° to 267°F, by exchange with boiler feed water.

About 90% of the NO_2-rich effluent gas from E-2 is recycled to SO_2 oxidizer D-1 to provide the necessary stoichiometric amount of NO_2 for the SO_2 oxidation and for the equimolar NO_2/NO absorption in E-1. The remaining 10% of the stripper overhead is sent to a single train nitric acid plant where the NO_x values from the flue gas are recovered as 60% nitric acid.

The purge of gas from the stripper at 272°F is cooled in C-3 to 105°F. A vapor-liquid separation is made in drum F-1, from which some 40 wt % (approx) HNO_3 condenses out and is pumped up via J-8 to 100 psia and fed to the HNO_3 absorption tower, E-3. The gas off F-1 is compressed to 105 psia in two-stage compressor J-6. Inter-stage cooling, vapor/liquid separation, and condensed HNO_3 recovery are carried out in C-4, F-2, and J-9 between the compressor stages. The gas exiting from the second compressor stage is at 351°F.

This gas is cooled to 166°F by exchanging heat with the tail gas from the HNO_3 absorber. Final gas cooling to 105°F occurs in Cooler C-6 and condensed acid removed in vapor/liquid separator F-3. Most of the HNO_3 is produced in absorption tower E-3 at 105°F and 100 psia. Sixty percent nitric acid can easily be produced in a standard nitric acid absorption tower containing bubble cap trays and cooling coils on each tray (C-9). The exothermic reaction is:

$$3NO_2 + H_2O = 2HNO_3 + NO \tag{4}$$

The presence of oxygen at a reasonable partial pressure, and the relatively low temperature, 105°F, affords substantial re-oxidation of NO to NO_2 in the absorber. Tail-gas from the absorption tower at 105°F and 90 psia is heated, by exchange with tower feed gas, to 301°F in C-5, then expanded from 90 to 16 psia through a power recovery turbine to deliver almost half of the horsepower needed to drive the feed gas compressor, J-6.

Nitric acid from E-3 is treated in HNO_3 bleacher E-4 at 15 psia by countercurrent contact with hot air. The latter is supplied by bleacher air compressor J-12, and steam heater C-8 which heats the bleacher air to 275°F. Spent bleacher air and the expanded tail gas are combined and recycled to the SO_2 oxidizer reactors.

The clean nitric acid from the bleacher is pumped to storage by J-11, first being cooled to 100°F in product acid cooler C-7. Sixty % nitric acid product amounts to 12,300 lbs/hr.

The process start-up involves the use of an initial inventory of stored liquid NO_2, which is bled into the SO_2 oxidizer as a flashed gas when the recovery plant is put on stream. The start-up inventory is replaced, whenever necessary, by purging a slip-stream of the HNO_3 absorption tower feed gas, and cooling to condense NO_2 via refrigeration unit L-3, and condenser C-10. A start-up steam heater, C-11, is used for heating up the large acid inventory as each train is brought on stream, initially, or after a shutdown.

2. Design Bases

The design bases for the process flowsheet are obtained primarily from information presented in TYCO Lab's final report, "Oxidation of SO_2".(1) Secondary references include the draft of TVA's report on the TYCO process (2), and use of certain M. W. Kellogg standards for process specifications. The important design bases are:

SO_2 Level in Flue Gas	0.261 mole %
NO_x Level in Flue Gas	500 ppm (vol)
as NO	95%
as NO_2	5%
SO_x Removal (as H_2SO_4)	90%
NO_x Removal (as HNO_3)	80%
Flue Gas Temperature	300°F
SO_2 Oxidizer-Reactor Residence Time	15 sec.
Scrubber Packed Height	30 ft
Scrubber Overhead Temperature	267°F
Scrubber Packing	3" Intalox Saddles
L/G in Scrubber	7 lb liq/lb gas
Catalytic Stripper Space Velocity	10 liq volumes Hr-Vol Activated Carbon
NO_2 Concentration off Stripper	10%
NO " " "	0.1%
Nitric Acid Plant Operating Pressure	100 psia
Nitric Acid Absorption Temperature	105°F
Nitric Acid Strength	60 wt %
Product Acids Storage	30 days
Sulfuric Acid Strength	80 wt %

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(1) Gruber, A., and Walitt, A. "Oxidation of SO_2" - Final Report, Contract CPA 70-59 for NAPCA, 1970

(2) TVA, " Sulfur Oxide Removal From Power Plant Stack Gases - TYCO Process", Preliminary Conceptual Design and Cost Study (Draft) Contract TV-29233A, 1/18/71.

3. Design Rationale

The rationale behind the design of the major equipment items and process sections is cited below:

D-1, SO_2 Oxidizer-Reactor

TYCO's data indicate that at least 15 seconds residence time is needed for the required oxidation of SO_2 to SO_3 at 300°F. The commercial reactor is assumed to operate under plug flow conditions, and that no gas mixing problems are encountered upon introduction of recycle NO_2 into the flue gas stream. It is assumed that a direct scale-up can be made from the TYCO bench-scale experimental results, and the 15 seconds residence time can be used to calculate the oxidizer volume.

E-1, N_2O_3 Scrubber

TYCO experimental work with $NO\text{-}NO_2$ absorption into hot 80% sulfuric acid was carried out in beds packed with 1/4 and 3/8" saddles at L/G's of 4 to 18 lb liquid/lb gas. The commercial scale flow sheet indicates scrubber operation in a tower packed with 3" saddles at an L/G of 7.7. The latter figure is approximately that L/G ratio suggested by TVA as the optimum for the overall process. For our case time did not permit optimization calculations to be made, so the value of 7.7 was selected as representative; it is within the range of the experimentation.

TYCO's miniplant scrubbing results indicate that the presently specified 98.2% N_2O_3 scrubbing efficiency would require about 30 feet of packing based on their 3/8" packing column; scaling up to 3-inch packing at the same liquid loading (in lb/hr-ft^2) would require more packed height to effect the same absorption efficiency. At the same L/G (7.7 lb/lb) the miniplant scrubber operated at L and G's of about 2100 and 270 lb/hr-ft^2 respectively, and would require about 30 ft of the 3/8" packing to achieve the desired absorption efficiency. The commercial scale scrubber is designed for liquid and gas loadings of 13,500 and 1750 lb/hr-ft^2, respectively. Very rough examination of general packed tower data indicate that, even with the less efficient larger packing (in terms of transfer unit heights), the large increase in liquid loading (2100 to 13,700) should cause the commercial scale tower to give the same scrubbing efficiency with 30 ft of packed height.

The scrubber, E-1, consists of four, 40 ft diameter units. It was assumed that a 40 ft diameter would be the largest vessel size practicable for a packed tower, and the number of vessels determined using a superficial gas velocity of about 500 ft/min.

E-2, Oxidizing Stripper

TYCO lab data showed that the best performance of the catalytic oxidizing stripper occurred at about 290°F with an L/G of about 16 and a space velocity of about 1 vol liquid/hr-vol catalyst. Close to 99% denitration stripping efficiency of NO_x was achieved. TYCO used a bed of granular activated carbon, 4 x 10 mesh, the largest commercially available activated carbon. This process evaluation also specifies the same grade (Witco 256).

Very optimistic conclusions had to be made about the performance of this catalytic stripper in order to obtain an overall reasonable process design. These are as follows:

1) A liquid-hourly-space velocity of 10 can be used to determine catalyst volume. TYCO attempted miniplant operation at an LHSV of 69, but failed. Using the demonstrated bench-scale LHSV of about 1 seems impractical for a commercial plant. It is assumed for the present design that this catalytic bed can be made to perform at a space velocity of 10.

2) Stripping efficiency will be 99% at 272°F with 99% of the NO_x stripped as NO_2, and 1% as NO with no N_2O formed.

3) Stripping air rate is set so as to give an overhead vapor of 10% NO_2. Such an NO_2 level is deemed necessary for reasonably economical nitric acid production downstream. Consequently, the resulting L/G for the stripper is fixed at about 165, 10-fold higher than the laboratory operation. It is assumed that the

stripping factor is sufficient to remove the NO_2 from the liquid acid. More air could be used to increase the stripping factor, if necessary, but this would decrease the overhead NO_2 concentration, which at 1% NO_2 seems to make the process unattractive.

4) The stripping reactor cross-sectional area was determined on the basis of roughly calculated flooding characteristics for a granular packed bed. The 4 x 10 mesh carbon has an average particle size range of about 1/4 to 1/16 inch. Crushed stone has a wetted packing factor of about 2190 for 1/4-inch size, and 1/4-inch carbon Raschig rings, about 1900. Optimistically, flooding characteristics for the granular carbon were assumed to be the same as for the 1/4-inch rings. The bed would flood at a G of about 80 lb/hr-ft^2 whereas TYCO operated at a G of around 6 lb/hr-ft^2. The commercial stripper was sized for a gas loading of 58 lb/hr-ft^2, or 70% of flooding. In order to have four trains, as in the scrubber section of the flow sheet, and to keep a maximum vessel diameter of about 40 feet, the strippers are specified as horizontal vessels 24 feet in diameter by 80 feet long. For comparison, four vertical vessels would have to be 48 feet in diameter.

HNO_3 Plant

A somewhat standard nitric acid absorption plant at 100 psia and 105° is specified for the recovery of NO_x as aqueous HNO_3. The purge rate of the 10% NO_2 from the catalytic stripper can be varied, as well as the nitric acid strength obtained by the absorption of NO_2 into water. The purge to the nitric acid plant was set on the basis that this stream should contain the stoichiometric amount of NO_2 to give the required HNO_3 production according to the reaction:

$$3NO_2 + H_2O = 2HNO_3 + NO$$

A purge with excess NO_2 would aid the absorption reaction, but at the expense of the HNO_3 plant handling a larger total volume of gas.

For the given purge rate, calculations were made to see what HNO_3 acid strength might reasonably be obtained. At 65%, the absorption approaches a pinch point, at which the number of tower trays is extremely large. Sixty percent acid, though, can be easily produced in a small tower.

L-1, Ash Removal Facilities

Fly ash which is not removed from the flue gas by the power plant electrostatic precipitator is picked up by the hot, sulfuric acid in scrubber, E-1. Approximately 20% of the ash is soluble in the acid; the remaining undissolved ash has to be removed from the circulating acid before being sent to the catalytic stripper for denitration. The undissolved ash in the 80% sulfuric acid will be about 0.005 wt % at 272°F. At this time, no definitive process design can be made in specifying the required ash removal equipment. A detailed study of solids/liquid separations at such low solids levels in the very corrosive acid medium is needed before any specifications can be made.

4. Process Appraisal

The TYCO process for SO_x and NO_x removal presents several inadequacies in terms of the soundness of the process definition. The major concern is the catalytic stripping operation. It is felt that this important denitration step has not been fully demonstrated at conditions suitable for scale-up to a commercial level. The experimental catalytic stripper gave the most favorable denitration results only at very low liquid space velocities (~1) at 290°F, and at a liquid to gas loading which is incompatible with the extremely high liquid circulation rate required for the upstream scrubbing operation. The commercial scale flow sheet has, of necessity, assumed operating conditions for the oxidizing stripper which have not been demonstrated in the laboratory. A continuous, integrated scrubbing/stripping operation has not been demonstrated; it was attempted unsuccessfully in the TYCO mini-plant runs.

Another problem with the catalytic stripper operation concerns the catalyst, the activated carbon. Experimentation has not verified catalyst life over 200 hours, and indications are that the carbon activity to catalyze the $HNSO_5$ oxidation is reduced by impurities in the acid. The commercial plant will have acid circulating with dissolved fly ash components, and some corrosion byproducts; the effect on the activated carbon performance must be investigated. There are some indications that the activated carbon manufacturers might be introducing larger sized carbon granules than the current maximum of 4 mesh. Experimentation should be carried out with the largest size activated carbon, since operating a packed bed of 1/8" granules under countercurrent liquid/gas flow presents flooding and pressure drop problems, with ensuing costly designs.

Some comments are made about the SO_2-oxidizer chemistry in section B of this report. Each stage of TYCO's experimentation indicates an upward trend in the required residence time for the flue gas in order to have 90% SO_2 oxidation. Early work indicated several seconds residence time; the latest TYCO data indicates about 20 seconds is required. Also, in the laboratory equipment the surface to volume ratio in the SO_2 reactor is very high compared to the duct type commercial reactor. The effects on the SO_2 oxidation caused by the possibility of small scale reactor behaving as a wetted-wall type device, owing to sulfuric acid condensing on the walls, would not be the same as in the low surface/volume commercial reactors. The residence time calculated in the small scale equipment might not be applicable on a larger scale.

The hot scrubbing operation seems to have been demonstrated experimentally at very high liquid scrubbing rates in the order of 800 lbs circulated per lb of sulfuric acid product. Further experimental work should be directed toward decreasing the very high scrubbing liquid rates as much as possible.

A major problem area in process definition concerns the ash/acid separation section of the flow sheet. As mentioned earlier, removal of this undissolved ash at levels of 0.005 wt % must be demonstrated, otherwise the overall process will be inoperable. Also, the disposition and effect on the process chemistry of the dissolved ash components in the system presents a problem which must be clarified experimentally.

The operability of this TYCO process presents unusual problems of process control. The NO/NO_2 ratio of 1 in the scrubber must be controlled very closely, since a high scrubbing efficiency (over 98%) is required. For example a 5% increase in the oxide ratio to 1.05 would decrease the overall NO_x removal from the flue gas from 80% to 25%. Of necessity, a power plant operates at fluctuating loads, depending on power demand. The process must be attuned to frequent turndowns and variations in NO_x and SO_x levels in the flue gas.

The TYCO Modified Chamber Process depends on the presence of both NO_x and SO_2 in the flue gas in order to effect removal of both. If upstream changes in boiler operation or fuel changes are made which tend to increase or decrease one of the oxide pollutants, there arises the possibility that the new system (at steady state conditions) may be one which does not recover the necessary SO_2 or NO_x to meet the pollution control requirements. Process control of the TYCO process is probably more crucial than for most other air pollution removal processes.

A final major item of concern in this process involves the partial pressure of sulfuric acid over the 80% acid solution. The equilibrium partial pressure of H_2SO_4 in the scrubber outlet gas is 66 ppm by volume, excluding any physically entrained acid, based on Gmitro and Vermeulen's data. This corresponds to 8.3 mg/SCF in the flue gas. Chemico, in its 1970 report for NAPCA, "Engineering Analysis of Emissions Control Technology for Sulfuric Acid Manufacturing Processes," states that a probable future maximum on H_2SO_4 emission will be about 3 mg/SCF. The gas effluent from the scrubber would have to be 225°F over 80% acid to have 3 mg H_2SO_4 vapor/SCF in the stack gas. However, at this low temperature, substantial water would be absorbed from the flue gas by the colder acid. It seems unlikely that future pollution control codes will allow one ton per hour H_2SO_4 emission into the atmosphere. This means that the TYCO process must be subjected to extensive modifications to reduce the sulfuric acid emitted with the stack gas.

REFERENCES

Gmitro, J. I., and Vermeulen, T., "Vapor-Liquid Equilibria for Aqueous Sulfuric Acid", UCRL-10886, Univ. Calif., Berkeley, June 24, 1963.

Oliver, E., "Sulfur Dioxide Removal From Stack Gases," SRI Report No. 63, July 1970.

Walitt, A., "A Process for the Manufacture of Sulfuric and Nitric Acids From Waste Flue Gases," Sec. Int'l Clean Air Congress of IUAPPA, Washington, D.C., Dec. 6-11, 1970.

——— "TYCO Process For Sulfuric Acid Production From Power Plant Flue Gases - Heat and Material Balance Analysis," Contract No. PH-86-68-92 for NAPCA by A. M. Kinney, Inc., March 31, 1969.

——— "Sulfur Oxide Removal From Power Plant Stack Gases - TYCO Process," Preliminary Conceptual Design and Cost Study (Draft) NAPCA Contract TV-29233A by TVA, Nov. 18, 1970.

B. CHEMISTRY

The following review of the chemistry of the process is based on Final Contract No. CPA 70-59 by A. Gruber and A. Walitt.(1) Basically the Tyco process removes SO_2 and NO from stack gas by reacting NO_2 with SO_2 and absorbing the resulting SO_3 and NO (with more NO_2) into hot (250-300°F) sulfuric acid. The advantage of the hot acid (approximately 80% sulfuric) is that there is no net absorption of steam from the flue gas and the gases do not have to be reheated for entrance to the stack.

Absorption of SO_2 and NO (For NO = 1/2 SO_2 in stack gas)

$$2H_2SO_4 + SO_2 + 1/2\ NO + 2\ 1/2\ NO_2 \text{ (added via recycle)}$$

$$\longrightarrow 3HNSO_5 + 1/2\ H_2O$$

Oxidizer

According to Tyco this is accomplished via the homogeneous gas phase oxidation of SO_2 with NO_2. They state that approximately 15-20 seconds are required in order to convert 90% of the SO_2. Therefore for a 1000 megawatt power station, an oxidizer volume of 750,000 to 1,000,000 ft^3 would be required. NO_2 and SO_2 concentrations in the gas are, as stated, about 6000 and 3000 ppm respectively, at about 300°F. Even this huge oxidizer volume would be optimistic if indeed the homogeneous gas phase reaction did control in view of the kinetic work of Boreskov and Illarionov (Zh. Fiz. Khim. Vol. 14, page 1428 (1940)) which indicates that at the 3000 to 6000 ppm concentration region the reaction rate would be infinitesimally slow.

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(1) Gruber, A., and Walitt, A., "Oxidation of SO_2" - Final Report, Contract CPA 70-5A For NAPCA, 1970.

N_2O_3 Absorber

The chemistry of this reaction is reasonably clear cut. Tyco data look reasonable. The reaction

$$NO + NO_2 + 2H_2SO_4 = 2HNSO_5 + H_2O$$

is well known. The absorber should be sized on gas film controlling mass transfer at appropriate liquid and gas loading rates. The only questionable item is the back pressure to be used (i.e. the proper equilibrium expression). The equilibrium expression used by Tyco is based on their own work and that of Berl and Saenger who both used vapor pressure measurements assuming that in the gas phase $NO = NO_2$. Their $NO + NO_2$ partial pressures are probably considerably higher than thermodynamic equilibrium due to the fact that they neglected any small amount of HNO_3 in the sulfuric acid solution (in fact, throughout their work they neglect it except for a few brief remarks). Even the presence of small amounts of HNO_3 in the acid solution along with $HNSO_5$ can elevate the partial pressure of N's above the solution by very large amounts. This is probably the reason why in the absorption experiments Tyco reports H_{OG}'s of about 8 feet which seems high (they probably had much higher back pressure in their absorption experiments than they thought they had). In general, Tyco's estimation of the size of the N_2O_3 absorber is felt to be conservative.

"Catalytic" Stripper

This catalytic stripper is an extremely important part of the process scheme. Nitrogen values absorbed into 250-300°F 80% sulfuric acid must now be stripped back into the gas phase at a high enough partial pressure to be able to make nitric acid product. The stripping efficiency must be high (approximately 99% N removal), carbon cannot be consumed, N_2O and N_2 cannot be produced and the "catalyst" must have a significant life.

In general, on the basis of Tyco's report it is almost impossible to design a commercial "catalytic stripper" since most of the experimentation was of an exploratory nature and did not provide careful material accounting.

Comments

1) Granular carbon (4 x 10 mesh) was used. This is certainly not a feasible commercial size for a reactor handling millions of pounds per hour of liquid and large volumes of gas.

2) "Catalytic" behavior has not been demonstrated. The highest $HNSO_5$ loading to the carbon bed (studied by passing 42,000 ml. of $HNSO_5$ solution to the bed) was approximately 4 g.moles/8 g.moles of carbon (30 in^3). The actual nitrogen oxides stripped amounted to about 2 g.moles/ 8 g.moles of carbon.

3) The carbon bed is apparently sensitive to impurities in the acid.

4) Only during two time periods (105 and 120 minutes, Table XXXII, page 131) was the nitrogen material balance better than 90%. The overall balance in this table is about 81%.

5) Only NO and NO_2 figures are given for the catalytic stripper exit gas. Since carbon is a reducing agent there is a definite possibility that the exit gas contains N_2, N_2O, CO, CO_2 and less possibly SO_2. It must be realized that in the overall scheme of stripping, if as little as 17% of the N's stripped appear as N_2 or N_2O there will be no net production of nitric acid in this proposed clean-up scheme. (The recycle ratio of NO_2 added per NO in the flue gas is high - 5/1). If larger than 17% then there will be a net purchase of NO_2 to remove the SO_2. To compound the problem, if CO or CO_2 is formed then carbon is being consumed.

Again, extrapolation of Sanfourche et al. data indicate that at 300°F and 80% acid with HNO_3 and $HNSO_5$ both in solution at a concentration of 0.023 g.moles/liter[a] the highest pressure of NO_2 obtainable, at a total pressure of 1.0 ata., is equal to 0.02 ata or 20,000 ppm , hardly a high enough pressure to make significant amounts of nitric acid in the nitric acid section of the plant.

Nitric Acid Production

This is a conventional nitric acid tower and can be sized in the conventional manner provided the "catalytic" stripper produces a high enough partial pressure of NO_2 and a high enough ratio of NO_2/NO. Since this unit (and also the catalytic stripper) does not handle the huge volumes of stack gas, increasing pressure may be advantageous.

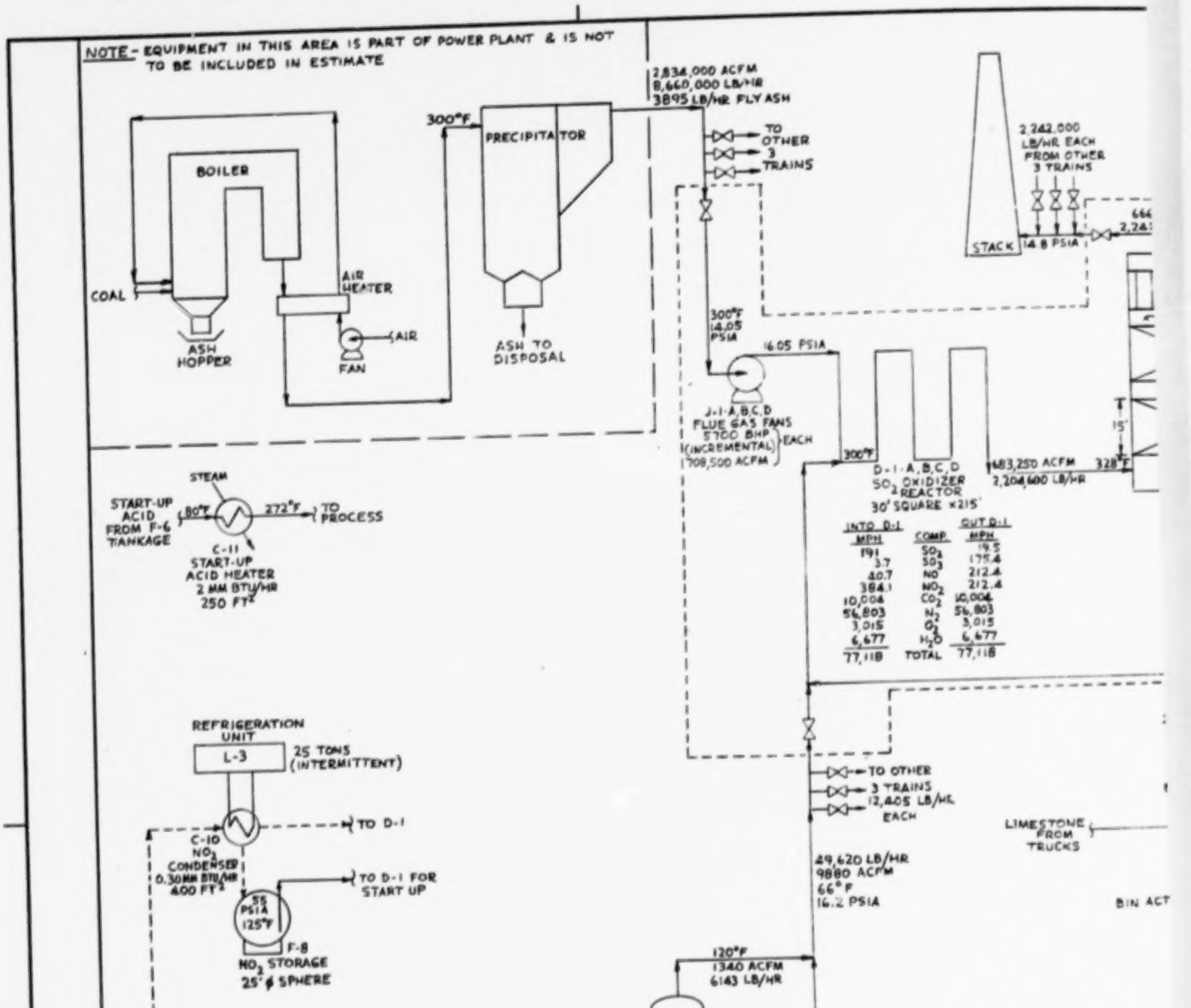
---

a) Tyco, Table XXXII, used 0.047 g.moles/liter of $HNSO_5$ in feed acid to stripper which we are going to assume is 0.023 g.moles/liter of $HNSO_5$ and 0.023 g.moles/liter of HNO_3 to see what the absolutely highest thermodynamic equilibrium pressure of NO_2 is above this solution.

An ultra-optimistic way to size the "catalytic stripper" would be to assume that true catalytic behavior is realized (i.e. there is no carbon consumption (no CO and CO_2), there is 100% selectivity in oxidizing $HNSO_5$ to NO_2 (no N_2 or N_2O formation), a long enough life to make carbon cost insignificant, and that large size activated carbon packing (1 or 2 inch rings, saddles, aggregate, etc.) can be effectively used instead of the 4 x 10 mesh that Tyco used. (Further, we make the assumption that oxidation is instantaneous - no kinetic or mass transfer limitation - which is an extreme simplification to say the least). In this case, sizing would then be based on the ability (stripping factor, VK/L) to strip NO_2 from an equimolar mixture of $HNSO_5$ and HNO_3, the most favorable stripping factor of all nitrogen components in the sulfuric acid.

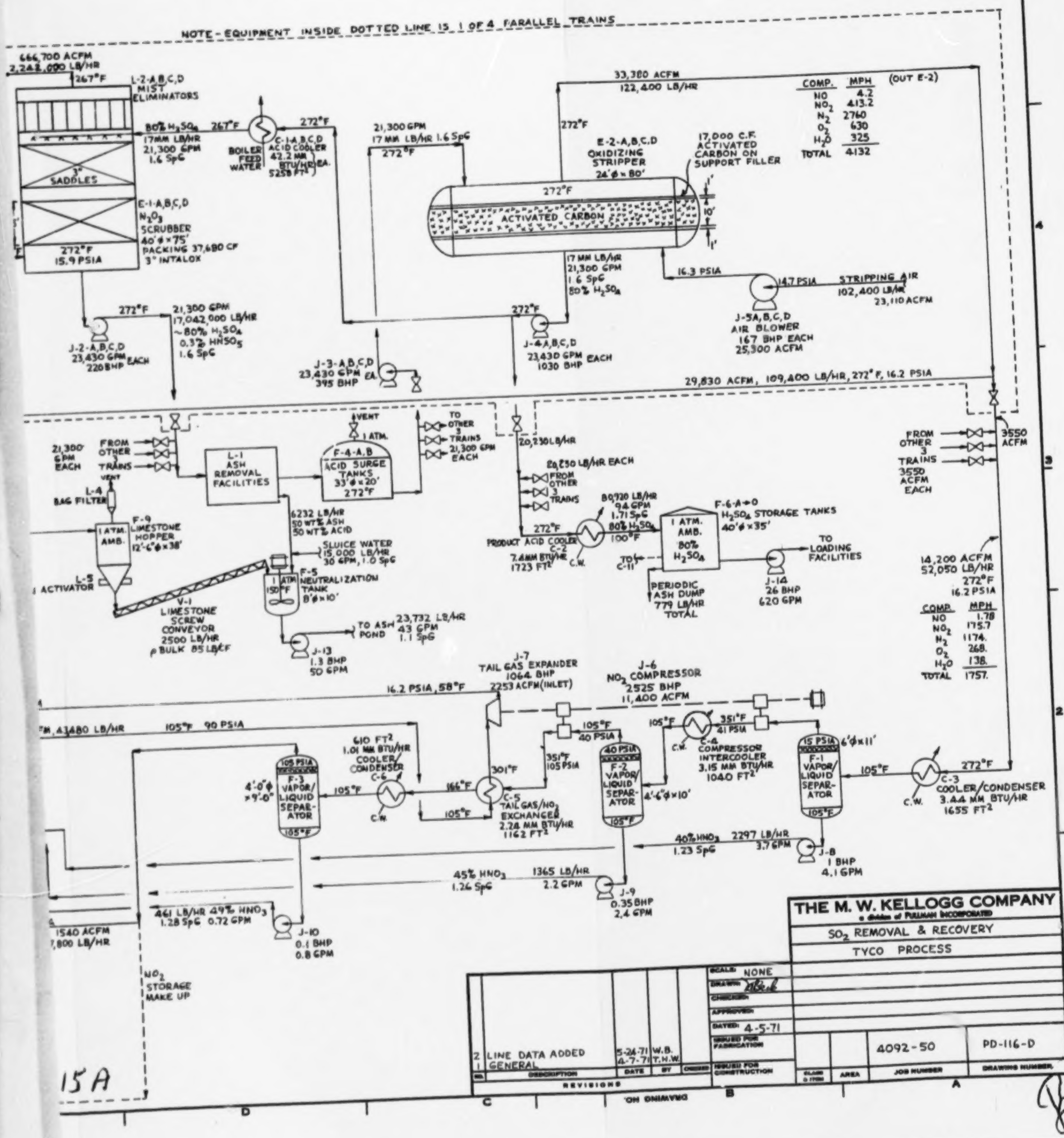
$$HNO_3\ (soln) + HNSO_5\ (soln) = 2NO_2(g) + H_2SO_4$$

Extrapolation of Literature data (Sanfourche and Rondier: Bull. Soc. Chim. France 43 (1928) 815) indicate that at 300°F and 80% H_2SO_4 a $VK/L = 2.0$ can be obtained at a liquid loading of $L = 1000$ lb acid/hr/ft^2 and a total gas loading of 1.5 lb moles/hr/ft^2 (Tyco's loading Table XXXII, page 131, was $L = 145$ lb/hr/ft^2 and $G_T = 0.29$ lb moles/hr/ft^2, for a $VK/L = 2.7$). Depending on size of carbon used the stripping tower can be ultra-optimistically sized on flooding velocities using a L/G of about 700 lbs/lb mole of gas.


NOTE - EQUIPMENT IN THIS AREA IS PART OF POWER PLANT & IS NOT TO BE INCLUDED IN ESTIMATE
BOILER
COAL
ASH HOPPER
AIR HEATER
FAN
AIR
300°F
PRECIPITATOR
ASH TO DISPOSAL
2,834,000 ACFM
8,660,000 LB/HR
3895 LB/HR FLY ASH
TO OTHER 3 TRAINS
2,242,000 LB/HR EACH FROM OTHER 3 TRAINS
STACK
14.8 PSIA
300°F
14.05 PSIA
16.05 PSIA
J-1-A,B,C,D FLUE GAS FANS 5700 BHP (INCREMENTAL) 708,500 ACFM EACH
300°F
D-1-A,B,C,D SO_2 OXIDIZER REACTOR 30' SQUARE × 215'
683,250 ACFM
2,204,600 LB/HR
328°F
15'
STEAM
START-UP ACID FROM F-6 TANKAGE
80°F
272°F
TO PROCESS
C-11 START-UP ACID HEATER 2 MM BTU/HR 250 FT²
REFRIGERATION UNIT
L-3
25 TONS (INTERMITTENT)
TO D-1
C-10 NO_2 CONDENSER 0.30 MM BTU/HR 400 FT²
TO D-1 FOR START UP
55 PSIA 125°F
F-8 NO_2 STORAGE 25' φ SPHERE
TO OTHER 3 TRAINS 12,405 LB/HR EACH
49,620 LB/HR
9880 ACFM
66°F
16.2 PSIA
LIMESTONE FROM TRUCKS
BIN ACT
120°F
1340 ACFM
6143 LB/HR
E-4 HNO_3 BLEACHER 2'-8"φ × 12' 3 TRAYS
43,480 LB/HR, 8510 ACFM
7.8 GPM
3871 LB/HR
WATER
105°F
1671 ACFM, 4
C-9 TRAY COOLING COILS 3.51 MM BTU/HR 1354 FT²
E-3 HNO_3 ABSORPTION 5'-6"φ × 24' 10 TRAYS
100 PSIA
105°F 154
47,800
105°F
100 PSIA
BLEACHER AIR 1390 ACFM 6143 LB/HR
14.7 PSIA
75°F
137°F
19.7 PSIA
J-12 43 BHP, 1410 ACFM BLEACHER AIR COMPRESSOR
STEAM
C-8 BLEACHER AIR HEATER 0.213 MM BTU/HR 77 FT²
275°F
17 PSIA
130°F
18.6 GPM
J-11 1.4 BHP 21 GPM
130°F
C-7 PRODUCT ACID COOLER 0.26 MM BTU/HR 243 FT²
C.W.
100°F
60% HNO_3 1.35 SpG
12,306 LB/HR, 18.3 GPM
105°F
PRODUCT ACID 12,306 LB/HR 60% HNO_3 18.4 GPM 1.34 SpG
1 ATM. 100°F 60% HNO_3
F-7-A,B,C,D HNO_3 STORAGE TANKS 35'φ × 32'
J-15 5 BHP 120 GPM
TO LOADING FACILITIES
21
H
G
F
E

INTO D-1 MPH	COMP.	OUT D-1 MPH
191	SO_2	19.5
3.7	SO_3	175.4
40.7	NO	212.4
384.1	NO_2	212.4
10,004	CO_2	10,004
56,803	N_2	56,803
3,015	O_2	3,015
6,677	H_2O	6,677
77,118	TOTAL	77,118

a


NOTE - EQUIPMENT INSIDE DOTTED LINE IS 1 OF 4 PARALLEL TRAINS
666,700 ACFM
2,242,000 LB/HR
267°F
L-2-A,B,C,D
MIST
ELIMINATORS
3" SADDLES
E-1-A,B,C,D
N_2O_3
SCRUBBER
40'ϕ × 75'
PACKING 37,680 CF
3" INTALOX
272°F
15.9 PSIA
80% H_2SO_4
17MM LB/HR
21,300 GPM
1.6 SpG
267°F
BOILER FEED WATER
C-1-A,B,C,D
ACID COOLER
42.2 MM BTU/HR EA.
5258 FT²
272°F
21,300 GPM
17 MM LB/HR 1.6 SpG
272°F
272°F
21,300 GPM
17,042,000 LB/HR
~80% H_2SO_4
0.3% $HNSO_5$
1.6 SpG
J-2-A,B,C,D
23,430 GPM EACH
220 BHP
J-3-A,B,C,D
23,430 GPM EA.
395 BHP
272°F
J-4 A,B,C,D
23,430 GPM EACH
1030 BHP
33,380 ACFM
122,400 LB/HR
272°F
E-2-A,B,C,D
OXIDIZING
STRIPPER
24'ϕ × 80'
17,000 C.F.
ACTIVATED
CARBON ON
SUPPORT FILLER
272°F
ACTIVATED CARBON
1'
10'
1'
17 MM LB/HR
21,300 GPM
1.6 SpG
80% H_2SO_4
16.3 PSIA
14.7 PSIA
STRIPPING AIR
102,400 LB/HR
23,110 ACFM
J-5A,B,C,D
AIR BLOWER
167 BHP EACH
25,300 ACFM
(OUT E-2)
29,830 ACFM, 109,400 LB/HR, 272°F, 16.2 PSIA
21,300 GPM EACH
FROM OTHER 3 TRAINS
VENT
L-4
BAG FILTER
F-9
LIMESTONE
HOPPER
12'-6"ϕ × 38'
1 ATM.
AMB.
L-5
ACTIVATOR
L-1
ASH
REMOVAL
FACILITIES
VENT
1 ATM.
F-4-A,B
ACID SURGE
TANKS
33'ϕ × 20'
272°F
TO OTHER 3 TRAINS
21,300 GPM EACH
6232 LB/HR
50 WT% ASH
50 WT% ACID
SLUICE WATER
15,000 LB/HR
30 GPM, 1.0 SpG
1 ATM
150°F
F-5
NEUTRALIZATION
TANK
8'ϕ × 10'
V-1
LIMESTONE
SCREW
CONVEYOR
2500 LB/HR
ρ BULK 85 LB/CF
TO ASH POND
23,732 LB/HR
43 GPM
1.1 SpG
J-13
1.3 BHP
50 GPM
20,230 LB/HR
20,230 LB/HR EACH
FROM OTHER 3 TRAINS
272°F
PRODUCT ACID COOLER
C-2
7.4 MM BTU/HR
1723 FT²
C.W.
80,920 LB/HR
94 GPM
1.71 SpG
80% H_2SO_4
100°F
F-6-A→D
H_2SO_4 STORAGE TANKS
40'ϕ × 35'
1 ATM.
AMB.
80%
H_2SO_4
TO C-11
PERIODIC
ASH DUMP
779 LB/HR
TOTAL
TO
LOADING
FACILITIES
J-14
26 BHP
620 GPM
FROM OTHER 3 TRAINS
3550 ACFM EACH
3550 ACFM
14,200 ACFM
52,050 LB/HR
272°F
16.2 PSIA
16.2 PSIA, 58°F
J-7
TAIL GAS EXPANDER
1064 BHP
2253 ACFM(INLET)
J-6
NO_2 COMPRESSOR
2525 BHP
11,400 ACFM
FM, 43480 LB/HR
105°F 90 PSIA
610 FT²
1.01 MM BTU/HR
COOLER/
CONDENSER
C-6
C.W.
105°F
166°F
301°F
105°F
C-5
TAIL GAS/NO_2
EXCHANGER
2.24 MM BTU/HR
1162 FT²
351°F
105 PSIA
105°F
40 PSIA
105 PSIA
F-3
VAPOR/
LIQUID
SEPAR-
ATOR
105°F
4'-0"ϕ
× 9'-0"
40 PSIA
F-2
VAPOR/
LIQUID
SEPAR-
ATOR
105°F
4'-6"ϕ × 10'
105°F
351°F
41 PSIA
C.W.
C-4
COMPRESSOR
INTERCOOLER
3.15 MM BTU/HR
1040 FT²
15 PSIA
6'ϕ × 11'
F-1
VAPOR/
LIQUID
SEPAR-
ATOR
105°F
105°F
272°F
C.W.
C-3
COOLER/CONDENSER
3.44 MM BTU/HR
1655 FT²
40% HNO_3
1.23 SpG
2297 LB/HR
3.7 GPM
J-8
1 BHP
4.1 GPM
45% HNO_3
1.26 SpG
1365 LB/HR
2.2 GPM
J-9
0.35 BHP
2.4 GPM
461 LB/HR 49% HNO_3
1.28 SpG 0.72 GPM
J-10
0.1 BHP
0.8 GPM
1540 ACFM
7,800 LB/HR
NO_2
STORAGE
MAKE UP

COMP.	MPH
NO	4.2
NO_2	413.2
N_2	2760
O_2	630
H_2O	325
TOTAL	4132

COMP.	MPH
NO	1.78
NO_2	175.7
N_2	1174.
O_2	268.
H_2O	138.
TOTAL	1757.

15A

THE M. W. KELLOGG COMPANY
a division of PULLMAN INCORPORATED

SO_2 REMOVAL & RECOVERY

TYCO PROCESS

SCALE: NONE
DRAWN:
CHECKED:
APPROVED:
DATED: 4-5-71
ISSUED FOR FABRICATION
ISSUED FOR CONSTRUCTION

NO.	DESCRIPTION	DATE	BY	CHKD
2	LINE DATA ADDED	5-24-71	W.B.	
1	GENERAL	4-7-71	T.H.W.	

REVISIONS

PLANT & ITEM	AREA	JOB NUMBER	DRAWING NUMBER
		4092-50	PD-116-D

MAGNESIUM OXIDE SCRUBBING PROCESS

A. PROCESS

1. Process Description (See MWK Dwg. No. PD-118-D)

Flue gas from the power plant at 300°F, together with the gases vented from the dryer of the regeneration system and the sulfuric acid plant, are cooled to 170°F in an indirect heat exchanger. The heat is recovered and used to reheat the absorber effluent gas from 120°F to 250°F before it is sent to the stack. The 170°F gases enter the venturi scrubber where a minimum of 98% of the ash is removed by a circulating stream of ash slurry in water.

In the scrubber enough water is evaporated to result in a saturated exit gas at 120°F. The ash is removed from the system in a slip stream which is discharged to a settling pond. Overflow water is pumped from the pond back into the circulating slurry to minimize the need for fresh water make-up.

As SO_3 dissolves in water forming H_2SO_4, limestone ($CaCO_3$) slurry is added to the discard stream to neutralize acid so formed.

The effluent gas from the venturi scrubber flows to a three stage absorber wherein the gas is contacted with a circulating stream of magnesium oxide/magnesium hydroxide slurry in water which is saturated with $MgSO_3$ (1.24%) and contains an appreciable quantity of dissolved $MgSO_4$. In the absorber a small amount of the SO_2 in the gas oxidizes to SO_3. All of the SO_3 and 95% of the SO_2 react with the magnesium oxide to form magnesium sulfite, which hydrates insoluble $MgSO_3 \cdot 6H_2O$, and magnesium sulfate, $MgSO_4$, which remains in solution.

The exit gas from the absorber is reheated to 250°F by the indirect heat exchange system previously described. From the exchanger the gas is discharged by the induced draft fan into the stack.

The concentration of solids in the absorber bottoms is held at 10% by the withdrawal of a slip stream to the magnesia regenerating system. The build-up of ash, which enters the absorber with the flue gas from the scrubber, is limited to 1% of the absorber bottoms by removal of the net ash from a portion of the stream of regenerated magnesia.

The slip stream to be regenerated is fed to a thickener where a clear solution is produced from the launder, and a bottoms of 30% solids content is withdrawn and fed to a centrifuge. The centrifuge reduces the solids to a cake containing 5% water, and the soluble salts associated with water. The clear liquor from the centrifuge, together with the thickener overflow, collects in the solution tank, from which part is returned directly to the absorber and the rest is used to slurry the reclaimed magnesium oxide/hydroxide.

The cake from the centrifuge is discharged into the cake hopper. The cake hopper also receives the dried magnesium sulfate recovered from the ash disposal system. The mixture of sulfate and wet centrifuge cake is then fed into the dryer. This dryer is of the direct fired type, preferably natural gas fuel with about 200% excess air to give an entering gas temperature of 1525°F. Flow from the dryer is countercurrent with the dried solids being heated to 500°F, a temperature sufficient not only to evaporate the free water but to drive off the water of hydration as well. The gases leave the dryer at 300°F, and after passing through a cyclone separator to recover any entrained dust, are discharged into the stream of flue gas entering the scrubber. Thus any dust that escapes the cyclone will be removed and any sulfur that may be in the dryer fuel will be recovered. The dryer effluent solids and the dust recovered by the cyclone are discharged into the calciner charge hopper.

Crushed green petroleum coke used for the reduction of $MgSO_4$ to $MgSO_3$ is received by truck and stored in the coke silo from where it is fed into the calciner charge hopper. As previously mentioned, this hopper also receives the discharge of dried solids from the dryer. The mixed solids from the hopper are discharged into the calciner.

The direct fired calciner uses natural gas fuel with about 100% excess air to obtain hot gases at 2240°F entering the kiln. In the kiln the flow is countercurrent, with the solids heated from 500° to 1600°F while the exit gas, including the SO_2 and CO_2 generated by the calcination, are at 600°F.

The gas from the calciner is vented to a spray tower for cooling, while the calcined solids, MgO plus ash, are discharged into the quench tank. In the quench tank, which is held at 180°F, sufficient fresh water is added to slake the oxide to hydroxide. This slaking is a slow reaction and is only partially completed in the course of the recirculation of the slurry to the absorber. The quench tank is provided with a vent stack in case a local high temperature zone at the 1600°F solids inlet into the liquid produces steam. The fresh water addition is via sprays in this stack which will condense and knock back any steam so formed. Liquid from the solution tank is added to the quench tank to dilute the slurry to the desired solids content. Temperature in the quench tank is maintained by circulation of a portion of the slurry through the external quench cooler. The ash discard stream also flows through the cooler and thence to the acid treating step at 120°F.

The net bottoms from the quench tank is transferred at 180°F to the surge tank where it is diluted to a 10% slurry. Make-up MgO and fresh water to balance the system losses are both added in this tank. The equilibrium temperature is 139°F but the slurry is cooled to 120°F in the solution cooler before it is returned to the absorber.

To prevent build-up of ash and other inert materials in the slurry, a continuous purge is required. This purge stream is taken from the quench tank and also contains $Mg(OH)_2$ in suspension and $MgSO_3$ and $MgSO_4$ in solution. These salts must be recovered to avoid excessive replacement requirement. After the addition of sufficient water from the base of the spray tower to balance evaporation loss, the discard stream is mixed with sulfuric acid (recycled from the acid plant) in stoichiometric quantity. The insoluble $Mg(OH)_2$ is converted to soluble $MgSO_4 \cdot 7H_2O$ which then dissolves leaving the ash in suspension. The slurry from the acidifying tank is pumped to the ash filter which separates the ash (and other solid inerts, if any) as a wet cake that is discharged into the ash slurry tank. The filtrate, a saturated (or nearly so) solution of $MgSO_4 \cdot 7H_2O$ with some $MgSO_3$ and $MgSO_4$ dissolved as well, is collected in the sulfate filtrate receiver from which it is pumped to a spray dryer.

The spray dryer is heated with 1200°F hot air produced by burning gas fuel at 300% excess air in the air heater. Here the solution is evaporated at 300°F to produce dry sulfate crystals which are returned to the scrubbing circuit via the sulfate reduction system. The effluent gases from the spray dryer flow through cyclones for dust recovery and then into the spray tower.

In the spray tower the gas from the calciner at 600°F, the gas from the spray drum at 300°F and the steam from the acidifying tank at 220°F are quenched with 110°F water thus cooling the gases to 120°F and condensing most of the water contained in the gases. The condensate is withdrawn at 180°F, pumped through an external cooler where it is cooled to 110°F, and split into three streams. The net recovered water is discharged to the surge tank, a stream is recycled to the acidifying tank to provide cooling, and the remainder is recirculated to the spray tower as quench water.

The cooled gases from the spray tower, containing 11.1% SO_2 are vented to the acid plant, which converts the SO_2 to 98% sulfuric acid. Vent gases from the acid plant containing unreacted SO_2 are recycled to the flue gas entering the scrubbing system. Storage tanks for 30 days net production of sulfuric acid are provided along with an unloading pump. A separate pump is provided to supply acid from storage to the ash acidifying tank.

Sulfur trioxide in the flue gas will be absorbed by the slurry circulating in the venturi scrubber case producing a weak solution of H_2SO_4 in the ash slurry stream. To neutralize this acid and thus prevent an excessive build-up of acid in the water circulated from the ash pond, facilities are provided for adding ground limestone ($CaCO_3$) to the ash discard stream. This will react with the acid to form $CaSO_4$ which is deposited in the pond along with the ash.

2. Design Bases

The present flow sheet developed for magnesium oxide scrubbing is for a new 1000 megawatt installation. General design criteria used in evaluating this process are the same as the basic criteria used for all the present evaluations and are given elsewhere in this report. Major design criteria specifically pertinent to the MgO process are listed below.

a) Six parallel scrubbing trains are provided including separate cooler, scrubber, reheater and induced-draft fan per train.

b) Shut-off gates are provided such that each train can be isolated from the other five.

c) Stack gas cooler and reheater system:indirect exchange against circulating water (with glycol added), single pass gas side cross-flow unit (12 identical units required -- 6 coolers and 6 reheaters).

d) Venturi scrubbers - 6 identical units (one per train), 98% ash removal, circulating and purge slurry @ 10% ash, design pressure drop @ 10" H_2O, vessel size: 34'-6" diameter by 66 ft high.

e) Scrubber (absorber) design (6 identical units required), UOP TCA contactors. Vessel size: 15 ft deep x 34 ft x 40 ft high with center partition (2 gas inlets and 2 gas outlets), 3 contacting stages of 1-1/2 inch plastic spheres; design pressure drop @ 9" H_2O; 95% SO_2 removal

(B&W data); bisulfite concentration of 0.762 wt % (as SO_2) in outlet slurry (B&W data).

f) Thickener - to concentrate outlet slurry from absorber from 10% solids to 30% solids; vessel size: 113 ft diameter and 10' high, 3 identical units.

g) Centrifuges - to separate solids from thickened slurry.

h) Dryer System - rotary dryers 16 ft dia x 200 ft, 2 identical units; to dry solids from centrifuges and drive off water of hydration; natural gas fuel, 200% excess air.

i) Calciner - rotary kilns 12.5 ft dia x 200 ft, 2 identical units, natural gas fuel, inlet temperature of 2240°F. To regenerate MgO for recycle by reduction with carbon and heat.

j) Acid Plant - to convert SO_2 liberated in calciner to concentrated H_2SO_4 which can be sold as a by-product.

k) Acid storage - storage capacity equivalent to 30 days' production is provided; unloading pumps are sized to pump out one day's production in 4 hours.

l) Equipment is provided to reduce MgO losses in the fly ash purge stream by converting insoluble $Mg(OH)_2$ to the soluble sulfate, filtering, and spray drying.

3. Design Rationale

The process design information specifically related to the MgO system was obtained from reports issued by The Babcock & Wilcox Company(1)(2). The general basic design criteria established for the present evaluations were used and the available B&W values prorated as needed. Where data were missing or not applicable to the present design, literature and/or vendor data were used if available, and when not available, assumptions were made as needed to complete the design. The judgment factors behind the major design bases are presented below.

a) Venturi Scrubber - used by B&W in their conceptual design. Most (98%) of the fly ash is removed in this vessel thereby reducing the possibility of plugging in the absorber and also providing an easier separation of the fly ash from the scrubbing slurry owing to the reduction in quantity of fly ash in the slurry.

b) Stack Gas Cooler-Reheater System - the indirect circulating water system was recommended by TVA based on a study of six different heat transfer schemes. The gas reheat temperature of 250°F also is based on TVA's recommendation.

c) Scrubber (Absorber) Design - based on B&W's experimental data for a floating bed absorber; UOP's TCA contactor was selected for the commercial plant. Flow rates, absorption efficiency, and pressure drop are based on B&W data (1).

d) Dryer - designed to dry the solids and drive off the water of hydration but the temperature is kept below that needed to decompose the magnesium sulfite. Natural gas fuel is used as the heat source and the gas temperature is regulated by the amount of excess air supplied with the combustion air.

e) Calciner - designed to regenerate the magnesium salts by thermally driving off SO_2 from the $MgSO_3$ while the $MgSO_4$ is reduced to MgO by reaction with carbon (coke) which is fed into the calciner along with the magnesium salts. The calciner temperature is a key parameter in that if it is too high the MgO produced will be unreactive (dead-burned), while the reduction reaction will not occur if the temperature is too low. A temperature in the range of 1100-1600°F appears necessary but the optimum has not yet been defined. For the present evaluation a temperature of 1100°F was assumed to insure good kinetics and reduce the size of the calciner.

f) Acid Plant - the SO_2 liberated during the regeneration of the MgO is used as the feed to a sulfuric acid plant for the recovery of sulfur as concentrated (~98%) acid. Unreacted SO_2 from the acid plant is recycled to the absorber. Storage capacity equivalent to 30 days' production of acid is provided to insure continuity of operation in case of short term interruptions of acid disposal (e.g., rail strikes, market fluctuations, etc.).

g) MgO Recovery System - the fly ash not removed in the venturi scrubber will be scrubbed out in the absorber, thus requiring a purge stream to avoid build-up of fly ash in the scrubbing slurry. To minimize MgO losses a recovery system is specified wherein the insoluble $Mg(OH)_2$ is converted to soluble $MgSO_4$ and the fly ash is separated by filtering. Sulfuric acid is recycled from the acid plant to react with the $Mg(OH)_2$ and the resulting $MgSO_4$ is recovered by spray drying and returned to the dryer-calciner circuit.

4. Process Appraisal

There is no complete process of this type presently in commercial operation. The Chemical Construction Corp's. process for acid plant gas, without particulate matter, apparently has been developed in detail. However no design operating conditions, or actual operating data were available for this evaluation. Therefore, a number of assumptions were required to develop the present flow sheet which should be considered as preliminary only.

The Babcock & Wilcox report (1) is concerned entirely with pilot plant experiments on particulate removal and the removal of SO_2 from the gas by MgO reaction. No experiments were reported on the regeneration of the sulfite.

The primary difficulty encountered by B&W in this laboratory work was formation of crystalline deposits, primarily $MgSO_3 \cdot 6H_2O$, with traces of $MgSO_4 \cdot H_2O$. If the bisulfite, $MgH_2(SO_3)_2$ exceeded about 1 gm/100 ml as SO_2 the deposition of crystals was extremely rapid. However the presence of fly ash in the solution apparently prevents deposition. The design under consideration assumes 0.9% fly ash in the absorber bottoms liquid (1.1% by weight of water alone). By B&W findings, this should be sufficient to eliminate deposits.

If this ash concentration is not high enough to prevent deposition, it may easily be increased by reducing the flow of the ash discard stream.

Another possible difficulty would be the accumulation of chlorides in the solution. These would be formed by reaction of HCl in the flue gas with $Mg(OH)_2 \cdot MgCl_2$ is quite soluble and does not decompose under heat. Since there is essentially no water lost from the regeneration system there is no way of purging the solution, so the build up could be to a point where precipitation would occur. This would be in the base of the absorber, the thickener, or the centrifuge. Solids formed there would be carried to the dryer and calciner, where at 712°C (1313°F) the crystals would melt and possibly cement the MgO at the quench point. The tubes of the quench cooler would collect deposits and plug. Resolution of this problem remains to be done.

Deactivation of the MgO by calcination may be a problem. B&W report that a temperature below 1100°F is advisable, and that at 2200°F the MgO is essentially unreactive. A more complete study of the mechanism of deactivation is requied, together with details of the exact temperature where deactivation starts. It is possible that the 1100°F quoted is a mass bed temperature resulting from severe local overheating, and that with careful application of heat appreciably higher temperatures can be withstood.

Also lacking is detailed information as to when the reduction of $MgSO_4$ to $MgSO_3$ by reaction with carbon will occur. It is presently estimated that 1600°F may be required, but it is possible that the reaction may proceed at a much lower temperature so that such severe calcining may not be necessary.

The use of a once-through direct fired calciner may not be advantageous as there is appreciable oxygen in the hot flue gas (100% excess air at 2240°F). There is a possibility that some or most of the coke added to reduce the sulfate may preferentially burn to CO_2 under these conditions, leaving the sulfate unchanged. A recirculation type calciner operated at very low excess air would eliminate this possible difficulty, and could provide a lower initial gas temperature. This would be advantageous in avoiding overburning of the magnesium oxide.

No data have been developed for the direct loss in the dryer and the calciner. The design presented herein assumes that dust entrainment with the exit gases will be minimal. A simple cyclone separator has been used to recover dust from the dryer off-gas while the dust from the calciner is to be recovered in the spray tower and returned to the system with the reclaimed water. If severe dust entrainment occurs in the calciner, a cyclone separator will be needed in the off-gas. However no information is readily available as to the type of crystals which will be formed in the absorber and the subsequent drying and calcining. If these materials are prone to entrainment, it may not be possible to employ direct fired apparatus for drying and calcining.

Erosion could be a major problem in the various circulating slurry streams. The use of rubber lined pumps and piping might be considered as a means of combating the combined corrosion-erosion problems.

REFERENCES

(1) Babcock & Wilcox "Magnesia Base Wet Scrubbing of Pulverized Coal Generated Flue Gas - Pilot Demonstration", NAPCA order 4152-01, September 28, 1970.

(2) Babcock & Wilcox "Conceptualized Fly-Ash and Sulfur Dioxide Scrubbing System with By-Product Recovery", Contract No. CPA 22-69-169.

MAGNESIUM OXIDE SCRUBBING

B. CHEMISTRY

System Description

Two reports have been submitted for comment: The Babcock and Wilcox Company "Magnesia Base Wet Scrubbing of Pulverized Coal Generated Flue Gas - Pilot Demonstration", dated Sept. 28, 1970; and a flow sheet and three pages of an untitled report from Chemical Construction Corporation.

The Babcock and Wilcox report describes the pilot plant removal of 95.5% to 99.2% of the sulfur dioxide and removal of 97.7% to 99.5% of the particulate matter. The Babcock and Wilcox system used a venturi type fly ash scrubber (water washing) and sulfur dioxide removal by venturi scrubbers and/or tray scrubbers using magnesium oxide slurry as absorbent for SO_2. The Babcock and Wilcox study did not include regeneration of the magnesium oxide.

The Chemical Construction Corporation pilot plant work was done on tail gas from a sulfuric acid plant (no particulate matter) and presents a schematic for the regeneration of the magnesium oxide. The Chemical Construction Corporation recovery system consists of centrifuging a portion of the $Mg(OH)_2$-$MgSO_3$ slurry, drying the $MgSO_3 \cdot 6 H_2O$ to remove water of hydration, calcination of the $MgSO_3$ to make MgO and SO_2 (concurrent calcination of any $MgSO_4$ with coke to convert sulfate to sulfite), recovery of SO_2 for production of sulfuric acid and recovery of MgO for recycle.

Comments - MgO Recovery System

The MgO recovery scheme, as per the Chemical Construction Corporation's schematic, is based on a SO_2-SO_3 feed that does not contain particulate matter (tail gas from a sulfuric acid plant).

Particulate matter and other inert materials may concentrate in the MgO recovery system and decrease the efficiency of the MgO system by adding to the burden of centrifuging, drying, calcining, etc.

Inert material may build up in the recovery system from several sources:

(1) A particulate scrubber working at 99.5% removal of particulate matter that processes 77,900 lbs fly ash/hour would leave 390 lbs particulate matter/hour available for possible collection in the $Mg(OH)_2$ slurry.

(2) The reduction of sulfate to sulfite with coke (assuming an ashless coke) will probably mean that excess coke will be used in the calcination and will be recycled with the MgO. The coke concentration in the slurry will probably stay at some steady

state level but will add to the inert content of the $Mg(OH)_2$ slurry.

(3) The regeneration of MgO does not mean the MgO will be reactive. Care must be taken during the regeneration to insure that inert MgO is not made. Babcock and Wilcox did not go into this point other than to comment in section 7.3-C, "The regenerated magnesia must be reactive to be reusable. Therefore, the thermal decomposition temperature should be minimized". And in section 5.4, "- - - - the optimum temperature for calcining is between 750 and 1100°F. Above calcining temperatures of about 2200°F, the resulting MgO is essentially unreactive and is referred to as Dead Burned - - - -".

Comments - Particulates in $Mg(OH)_2$ Slurry

Large amounts of particulate material in the $Mg(OH)_2$ slurry are undesirable; however, small amounts of particulate matter in the $Mg(OH)_2$ slurry are advantageous in that they have been found to decrease the rate of deposition of $MgSO_3 \cdot 6H_2O$ on the scrubber surfaces due to a slight abrasive action of the particles and large particulate surface areas for crystal growth.

Comments - Venturi Particulate Scrubber

The venturi particulate scrubber removed 97.7% to 99.5% of the particulate matter and none of the sulfur dioxide. The aqueous slurry of particulate matter was recirculated through the venturi, a portion of the slurry was discarded, and de-ionized water was used for make-up. The pH of the slurry was 2 to 3.5.

The sulfur content of the slurry is not reported but it appears that the slurry is absorbing sulfuric acid and/or bisulfate.

The used particulate slurry is being dumped in the Babcock-Wilcox scheme and is not useable in the Chemical Construction Corporation regeneration scheme.

An advantage may be gained by a more efficient particulate scrubber in that it would permit less particulates to accumulate in the MgO recovery system and would decrease the amount of sulfate that would need to be reduced with coke in the calcination step. The calcination might then be accomplished at lower temperature and shorter times and yield a more reactive magnesium oxide.

Comments - Gas Scrubbers

The venturi gas scrubber and tray gas scrubber were designed to remove sulfur dioxide but both are very efficient ($>$ 98% removal) in removing particulate matter from the gas stream. A small amount of particulate matter will not be trapped by the particulate scrubber during normal operation and may find its way into the MgO recovery system. A failure in the venturi particulate scrubber (i.e., failure of water-slurry circulating pump) would cause a rapid buildup of ash particles in the MgO recovery system.

The MgO recovery system is a closed system and does not make provision for discharge of inert materials that may build up in the $Mg(OH)_2$ slurry.

Reaction - Slaking

Fresh or recovered magnesium oxide is slaked with water to produce magnesium hydroxide

$$MgO + H_2O \longrightarrow Mg^{++} + 2OH^- \qquad \text{(Eq. 1)}$$

$$Mg^{++} + 2OH^- \rightleftharpoons Mg(OH)_2(S) \qquad \text{(Eq. 2)}$$

Two to three hours at 180°F were required to convert 94.9% of a reactive MgO to $Mg(OH)_2$.

Babcock and Wilcox determined that MgO and $Mg(OH)_2$ had the same ability to absorb sulfur dioxide.

Reaction - Formation of Sulfate

The presence of sulfate in the recovery system is undesirable since an additional treatment is required to reduce the sulfate to sulfite.

Sulfite may be oxidized to sulfate by several mechanisms, either in gas phase or in the slurry; by reaction with excess air in the flue gas or with oxygen dissolved in make-up water,

$$SO_3^{=} + 1/2\ O_2 \longrightarrow SO_4^{=} \qquad (Eq.\ 3)$$

or by reaction with nitrogen oxides from the flue gas.

$$NO_2 + SO_3^{=} \longrightarrow NO + SO_4^{=} \qquad (Eq.\ 4)$$

The sulfate present will react with magnesium in the slurry to form magnesium sulfate

$$Mg^{++} + SO_4 \xrightarrow{HOH} MgSO_4 \cdot 7H_2O \qquad (Eq.\ 5)$$

The reactions in Eq. 3, 4 and 5 are rapid and may occur anywhere from in the furnace to in the $Mg(OH)_2$ absorber.

Reaction - Absorbing Sulfur Dioxide

The overall reaction for the removal of sulfur dioxide with MgO is

$$MgO + SO_2 \xrightarrow{H_2O} MgSO_3 \cdot 6H_2O(S) \qquad (Eq.\ 6)$$

in which sulfur dioxide is absorbed in aqueous MgO slurry to make bisulfite and sulfite.

$$SO_2 + OH^- \longrightarrow HSO_3^- \qquad (Eq.\ 7)$$

$$HSO_3^- + OH^- \rightleftharpoons SO_3^{=} + HOH \qquad (Eq.\ 8)$$

The sulfite will react with the magnesium in the slurry to precipitate $MgSO_3 \cdot 6H_2O$.

$$SO_3^{=} + Mg^{++} \xrightarrow{H_2O} MgSO_3 \cdot 6H_2O \downarrow \qquad (Eq.\ 9)$$

The dissolution of MgO with water (Eq. 1) is the slowest and would be the rate setting step. The rate of dissolution of MgO in the slurry is enhanced by the buffering effect of the sulfite-bisulfite system (Eq. 7 and 8). The enhancement of the rate of solubility of MgO is such that Babcock and Wilcox report MgO and $Mg(OH)_2$ had the same ability to absorb sulfur dioxide.

Reaction - Absorption Stoichiometry

Babcock and Wilcox report that using a reactive MgO, that had not been recycled, one mole of MgO was required to absorb one mole of sulfur dioxide.

Reaction - Absorption pH

The pH of the system was controlled by regulation of the MgO makeup.

At pH more acid than 7 the sulfur dioxide absorption decreased and high sulfate levels had an adverse effect on the sulfur dioxide absorption. At pH more basic than 7 the rate of sulfur dioxide absorption was constant and the sulfate level had no effect on sulfur dioxide absorption.

Reaction - Absorption-MgO Coating

The MgO base system (as opposed to the CaO base system) is not dependent on the available surface area of the MgO. The solubility of magnesium sulfite is high as compared to the solubility of calcium sulfite (485 mole/mole @ 140°F) and does not tend to coat the MgO.

Reaction - Absorption-Nitrogen Oxides

Nitrogen oxides are not absorbed by the MgO slurry system as described. Babcock and Wilcox suggest an additional MgO absorber and injection of recycled NO_2 to remove NO from the flue gas.

Reaction - Calcination and Sulfate Reduction

The calcination process is to convert dehydrated magnesium sulfite to sulfur dioxide gas and make active magnesium oxide for recycle.

$$MgSO_3 \longrightarrow MgO + SO_2 \uparrow \qquad \text{(Eq. 10)}$$

The dehydrated solids fed to the calcination contain magnesium sulfate which is reduced with coke to sulfite.

$$2MgSO_4 + C \longrightarrow 2MgSO_3 + CO_2 \uparrow \qquad \text{(Eq. 11)}$$

The activity of the MgO produced by the calcination (Eq. 10) will be critical.

Chemical Construction Corporation make no mention of the activity of the produced MgO, calcination temperature, calcination time, quantity of carbon used in calcination, disposition of any excess of carbon. The only hint in regard to the calcination is that it is done at less than atmospheric pressure.

SUMMARY

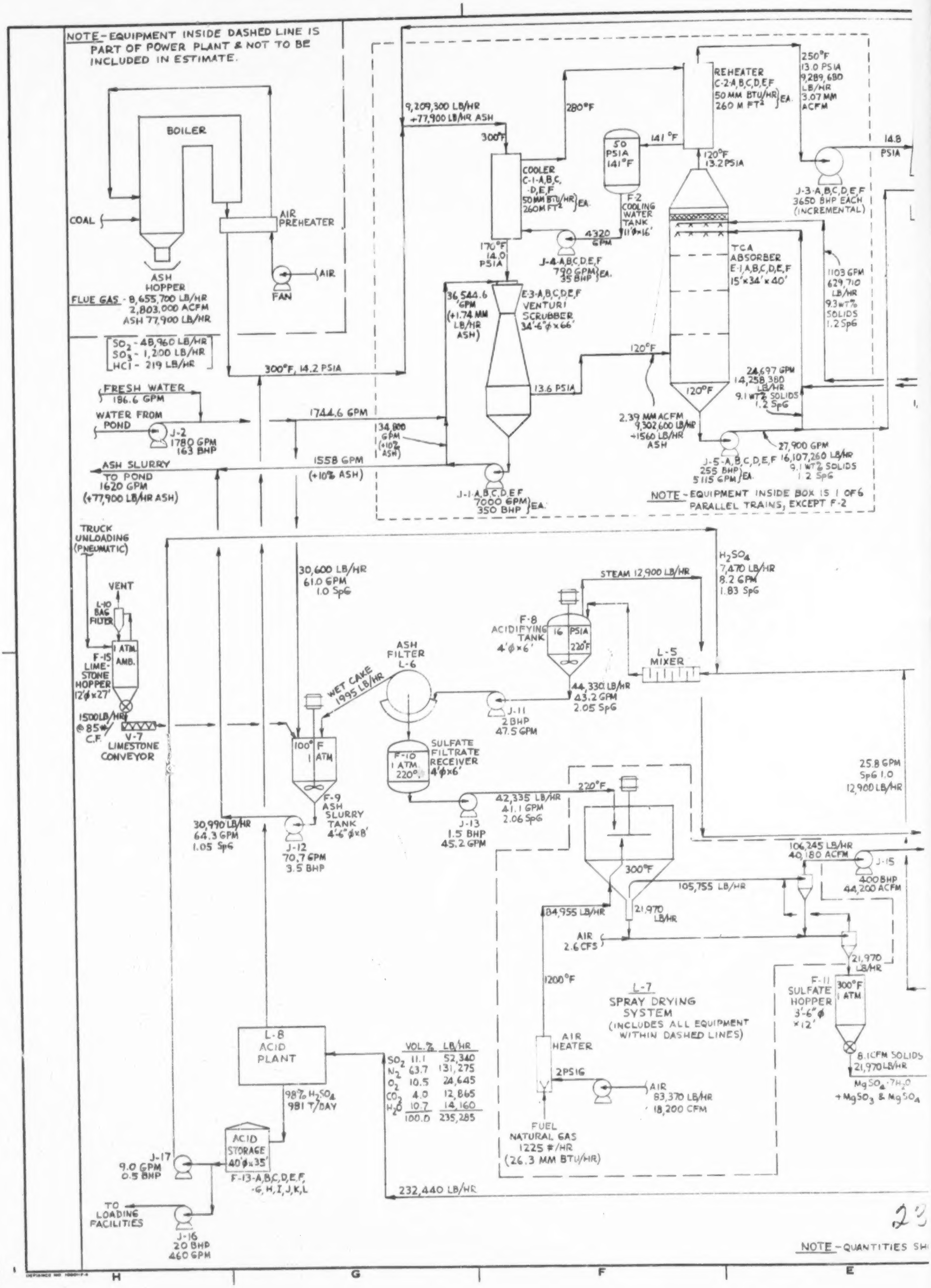
The chemistry of the removal of sulfur dioxide with MgO slurry appears to be quite workable and, in fact, has been done on pilot plant scale.

The undefined areas appear to be:

(1) Does the recovery system produce an active MgO for recycle?

(2) How much inert material can the recovery system tolerate?

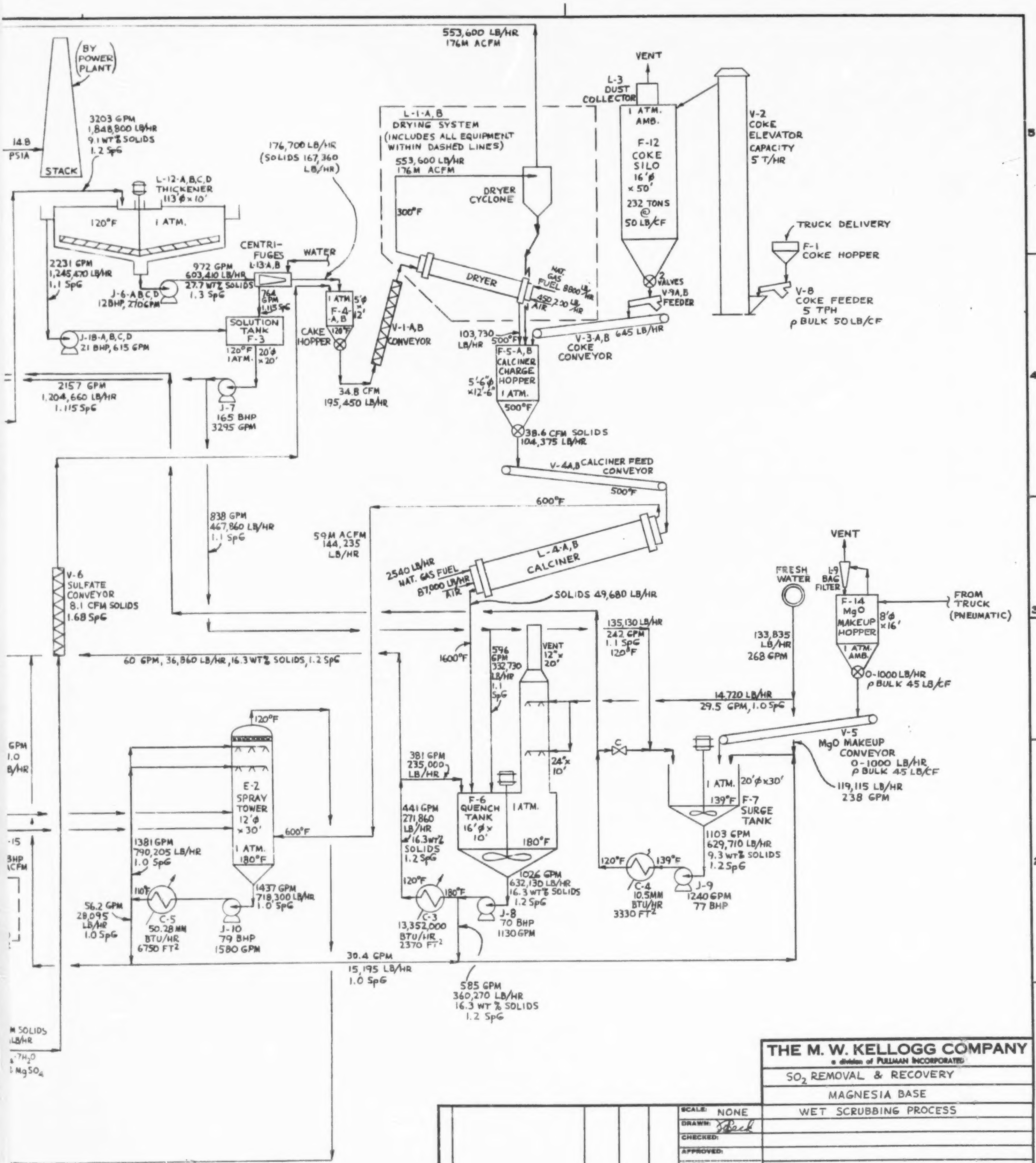
NOTE- EQUIPMENT INSIDE DASHED LINE IS PART OF POWER PLANT & NOT TO BE INCLUDED IN ESTIMATE.


BOILER
COAL
ASH HOPPER
AIR PREHEATER
FAN
AIR
FLUE GAS - 8,655,700 LB/HR
2,803,000 ACFM
ASH 77,900 LB/HR
SO2 - 48,960 LB/HR
SO3 - 1,200 LB/HR
HCl - 219 LB/HR
300°F, 14.2 PSIA
FRESH WATER
186.6 GPM
WATER FROM POND
J-2
1780 GPM
163 BHP
1744.6 GPM
ASH SLURRY TO POND
1620 GPM
(+77,900 LB/HR ASH)
1558 GPM
(+10% ASH)
134,800 GPM (+10% ASH)
J-1-A,B,C,D,E,F
7000 GPM
350 BHP EA.
9,209,300 LB/HR
+77,900 LB/HR ASH
300°F
280°F
COOLER
C-1-A,B,C,D,E,F
50 MM BTU/HR
260 M FT² EA.
170°F
14.0 PSIA
36,544.6 GPM
(+1.74 MM LB/HR ASH)
E-3-A,B,C,D,E,F
VENTURI SCRUBBER
34'-6"ϕ x 66'
13.6 PSIA
120°F
50 PSIA
141°F
F-2
COOLING WATER TANK
11'ϕ x 16'
4320 GPM
J-4-A,B,C,D,E,F
790 GPM
35 BHP EA.
141°F
REHEATER
C-2-A,B,C,D,E,F
50 MM BTU/HR
260 M FT² EA.
120°F
13.2 PSIA
250°F
13.0 PSIA
9,289,680 LB/HR
3.07 MM ACFM
J-3-A,B,C,D,E,F
3650 BHP EACH
(INCREMENTAL)
14.8 PSIA
TCA ABSORBER
E-1-A,B,C,D,E,F
15'x34'x40'
1103 GPM
629,710 LB/HR
9.3 WT% SOLIDS
1.2 SpG
24,697 GPM
14,258,380 LB/HR
9.1 WT% SOLIDS
1.2 SpG
120°F
2.39 MM ACFM
9,302,600 LB/HR
+1560 LB/HR ASH
J-5-A,B,C,D,E,F
255 BHP
5115 GPM EA.
27,900 GPM
16,107,260 LB/HR
9.1 WT% SOLIDS
1.2 SpG
NOTE - EQUIPMENT INSIDE BOX IS 1 OF 6 PARALLEL TRAINS, EXCEPT F-2
TRUCK UNLOADING (PNEUMATIC)
VENT
L-10 BAG FILTER
1 ATM. AMB.
F-15 LIME-STONE HOPPER
12'ϕ x 27'
1500 LB/HR @ 85# C.F.
V-7 LIMESTONE CONVEYOR
30,600 LB/HR
61.0 GPM
1.0 SpG
WET CAKE 1995 LB/HR
ASH FILTER L-6
100°F
1 ATM
F-9 ASH SLURRY TANK
4'-6"ϕ x 8'
30,990 LB/HR
64.3 GPM
1.05 SpG
J-12
70.7 GPM
3.5 BHP
J-11
2 BHP
47.5 GPM
F-8 ACIDIFYING TANK
4'ϕ x 6'
16 PSIA
220°F
44,330 LB/HR
43.2 GPM
2.05 SpG
STEAM 12,900 LB/HR
H2SO4
7,470 LB/HR
8.2 GPM
1.83 SpG
L-5 MIXER
F-10
1 ATM.
220°
SULFATE FILTRATE RECEIVER
4'ϕ x 6'
J-13
1.5 BHP
45.2 GPM
42,335 LB/HR
41.1 GPM
2.06 SpG
220°F
300°F
25.8 GPM
SpG 1.0
12,900 LB/HR
106,245 LB/HR
40,180 ACFM
J-15
400 BHP
44,200 ACFM
105,755 LB/HR
84,955 LB/HR
21,970 LB/HR
AIR
2.6 CFS
21,970 LB/HR
F-11 SULFATE HOPPER
3'-6"ϕ x 12'
300°F
1 ATM
6.1 CFM SOLIDS
21,970 LB/HR
MgSO4·7H2O
+MgSO3 & MgSO4
1200°F
L-7
SPRAY DRYING SYSTEM
(INCLUDES ALL EQUIPMENT WITHIN DASHED LINES)
AIR HEATER
2 PSIG
AIR
83,370 LB/HR
18,200 CFM
FUEL
NATURAL GAS
1225 #/HR
(26.3 MM BTU/HR)
L-8
ACID PLANT
98% H2SO4
981 T/DAY
232,440 LB/HR
ACID STORAGE
40'ϕ x 35'
F-13-A,B,C,D,E,F,G,H,I,J,K,L
J-17
9.0 GPM
0.5 BHP
TO LOADING FACILITIES
J-16
20 BHP
460 GPM
H
G
F
E
23

	VOL.%	LB/HR
SO_2	11.1	52,340
N_2	63.7	131,275
O_2	10.5	24,645
CO_2	4.0	12,865
H_2O	10.7	14,160
	100.0	235,285

NOTE - QUANTITIES SH

a.



(BY POWER PLANT)
STACK
14.8 PSIA
3203 GPM
1,848,800 LB/HR
9.1 WT% SOLIDS
1.2 SpG
L-12-A,B,C,D THICKENER 113'ϕ × 10'
120°F
1 ATM.
2231 GPM
1,245,470 LB/HR
1.1 SpG
J-6-A,B,C,D
12 BHP, 2706 GPM
972 GPM
603,410 LB/HR
27.7 WT% SOLIDS
1.3 SpG
CENTRI-FUGES L-13-A,B
WATER
764 GPM
1.115 SpG
SOLUTION TANK F-3
120°F
1 ATM.
20'ϕ × 20'
J-18-A,B,C,D
21 BHP, 615 GPM
176,700 LB/HR
(SOLIDS 167,360 LB/HR)
1 ATM
F-4-A,B
120°F
5'ϕ × 12'
CAKE HOPPER
V-1-A,B CONVEYOR
34.8 CFM
195,450 LB/HR
2157 GPM
1,204,660 LB/HR
1.115 SpG
J-7
165 BHP
3295 GPM
553,600 LB/HR
176M ACFM
L-1-A,B
DRYING SYSTEM
(INCLUDES ALL EQUIPMENT WITHIN DASHED LINES)
553,600 LB/HR
176M ACFM
DRYER CYCLONE
300°F
DRYER
NAT. GAS FUEL 8800 LB/HR
450,200 LB/HR AIR
103,730 LB/HR
500°F
F-5-A,B
CALCINER CHARGE HOPPER
1 ATM.
500°F
5'-6"ϕ × 12'-6"
38.6 CFM SOLIDS
104,375 LB/HR
VENT
L-3 DUST COLLECTOR
1 ATM. AMB.
F-12
COKE SILO
16'ϕ × 50'
232 TONS @ 50 LB/CF
2 VALVES
V-9A,B FEEDER
V-3-A,B
COKE CONVEYOR
645 LB/HR
V-2
COKE ELEVATOR
CAPACITY 5 T/HR
TRUCK DELIVERY
F-1
COKE HOPPER
V-8
COKE FEEDER
5 TPH
ρ BULK 50 LB/CF
V-4A,B CALCINER FEED CONVEYOR
500°F
600°F
838 GPM
467,860 LB/HR
1.1 SpG
59M ACFM
144,235 LB/HR
2540 LB/HR NAT. GAS FUEL
87,000 LB/HR AIR
L-4-A,B
CALCINER
SOLIDS 49,680 LB/HR
V-6
SULFATE CONVEYOR
8.1 CFM SOLIDS
1.68 SpG
60 GPM, 36,860 LB/HR, 16.3 WT% SOLIDS, 1.2 SpG
1600°F
596 GPM
332,730 LB/HR
1.1 SpG
VENT
12" × 20'
24" × 10'
135,130 LB/HR
242 GPM
1.1 SpG
120°F
FRESH WATER
133,835 LB/HR
268 GPM
14,720 LB/HR
29.5 GPM, 1.0 SpG
VENT
L-9 BAG FILTER
F-14
MgO MAKEUP HOPPER
8'ϕ × 16'
1 ATM. AMB.
FROM TRUCK (PNEUMATIC)
0-1000 LB/HR
ρ BULK 45 LB/CF
V-5
MgO MAKEUP CONVEYOR
0-1000 LB/HR
ρ BULK 45 LB/CF
119,115 LB/HR
238 GPM
C
1 ATM.
20'ϕ × 30'
139°F
F-7
SURGE TANK
1103 GPM
629,710 LB/HR
9.3 WT% SOLIDS
1.2 SpG
120°F
139°F
C-4
10.5MM BTU/HR
3330 FT²
J-9
1240 GPM
77 BHP
120°F
E-2
SPRAY TOWER
12'ϕ × 30'
1 ATM.
180°F
600°F
1381 GPM
790,205 LB/HR
1.0 SpG
110°F
56.2 GPM
28,095 LB/HR
1.0 SpG
C-5
50.28 MM BTU/HR
6750 FT²
J-10
79 BHP
1580 GPM
1437 GPM
718,300 LB/HR
1.0 SpG
381 GPM
235,000 LB/HR
441 GPM
271,860 LB/HR
16.3 WT% SOLIDS
1.2 SpG
F-6
QUENCH TANK
16'ϕ × 10'
1 ATM.
180°F
120°F
180°F
C-3
13,352,000 BTU/HR
2370 FT²
J-8
70 BHP
1130 GPM
1026 GPM
632,130 LB/HR
16.3 WT% SOLIDS
1.2 SpG
30.4 GPM
15,195 LB/HR
1.0 SpG
585 GPM
360,270 LB/HR
16.3 WT% SOLIDS
1.2 SpG
GPM
1.0
B/HR
-15
BHP
CFM
M SOLIDS
LB/HR
·7H₂O
MgSO₄

THE M. W. KELLOGG COMPANY
a division of PULLMAN INCORPORATED

SO$_2$ REMOVAL & RECOVERY
MAGNESIA BASE
WET SCRUBBING PROCESS

SCALE: NONE
DRAWN: Beck
CHECKED:
APPROVED:
DATED: 4-26-71
ISSUED FOR FABRICATION
ISSUED FOR CONSTRUCTION

CLASS & ITEM	AREA	JOB NUMBER	DRAWING NUMBER
		4092-50	PD-118-D

NO.	DESCRIPTION	DATE	BY	CHECKED
2	GENERAL	5-18-71	W.B.	
1	ADD QUANTITIES	5-4-71	W.B.	

REVISIONS

DRAWING NO.

235-H

TIES SHOWN ARE TOTALS FOR ALL PARALLEL UNITS.

D C B A

ZINC OXIDE PROCESS FOR REMOVING SO_2 FROM STACK GASES

A. PROCESS

1. Process Description (See MWK Dwg No. PD-110-D)

The major reactions involved in the zinc oxide process are summarized below.

Scrubbing Reaction

$$Na_2SO_3 + H_2O + SO_2 = 2NaHSO_3$$
$$Na_2SO_3 + 1/2\ O_2 = 2Na_2SO_4$$

Liming Tanks

$$2NaHSO_3 + CaO = Na_2SO_3 + CaSO_3 + H_2O$$

Gasifier

$$CaSO_3 + SO_2 + H_2O = Ca(HSO_3)_2$$
$$Ca(HSO_3)_2 + Na_2SO_4 = CaSO_4 + 2NaHSO_3$$

Mixer

$$2NaHSO_3 + ZnO = ZnSO_3 + Na_2SO_3 + H_2O$$

Calciner

$$ZnSO_3 = ZnO + SO_2$$

In the zinc oxide process, stack gas is scrubbed with an aqueous solution of sodium sulfite-bisulfite. The spent solution is mixed in a clarifier with a slurry of calcium sulfite in an aqueous solution of sodium bisulfite. The thickened calcium sulfite-fly ash slurry from the clarifier is next reacted in a gasifier with sulfur dioxide whereby the calcium sulfite is solutized as calcium hydrogen sulfite. Sulfate ions that are present in the gasifier precipitate out as calcium sulfate. Waste solids of fly ash and calcium sulfate from the gasifier are discarded and the soluble portion is reacted with lime (CaO) to form the insoluble calcium sulfite needed for mixing with the spent absorber solution.

The supernatant liquid from the clarifier is reacted in a mixer with zinc oxide to give insoluble zinc sulfite. The resulting lean solution from the mixer is refortified with soda ash to make up for losses and this solution is sent back to the stack gas scrubber. Zinc sulfite is processed by drying off the excess water and then indirectly calcining to give zinc oxide and sulfur dioxide. Zinc oxide is recycled back to the mixing vessel while part of the sulfur dioxide is used in the gasifier with the remainder sent to an acid plant for recovery of the sulfur values as 98.5% sulfuric acid.

2. Process Design Basis

This process has been evaluated for operation with a new 1000 MW power plant. General design criteria used in evaluating this process are those given elsewhere in this report as the basic criteria for all the present evaluations. Design criteria related specifically to the zinc oxide process are based on the flow sheet presented in a report by Envirogenics (1) to the National Air Pollution Control Administration (NAPCA). Process flows and equipment sizes have been scaled to the specified plant size (1000 MW) and adjusted for the sulfur level used in this evaluation.

Since the zinc oxide process uses aqueous scrubbers, it was assumed that mechanical separators would remove 80% of the fly ash and the scrubbers would remove the remainder, thereby eliminating the need for electrostatic precipitators. A stack gas cooler-reheater system has been added to the process so that the treated stack gas is reheated to get plume rise.

Sulfur dioxide removed in the zinc oxide process is recovered as 98.5 percent sulfuric acid. The equipment and processing cost for converting the sulfur dioxide to sulfuric acid has been included in this evaluation.

Other design criteria related to the zinc oxide process are discussed in more detail in the following section, viz., Process Design Rationale.

3. Process Design Rationale

The evaluation of the zinc oxide process is based on the process flow sheet given in a 1970 report submitted to the National Air Pollution Control Administration by Envirogenics (1). A 1400 MW new power plant was the basis of the material balance prepared and the equipment sized by Envirogenics; the material balance was adjusted to the process design basis used by Kellogg. The assumptions made and the design criteria used for evaluation of the zinc oxide process are discussed in detail below.

Stack gas flows through cyclone separators where 80% of the fly ash is removed. The remaining fly ash in the flue gas will be removed in the stack gas scrubbers and is slurried with the scrubbing solution. Therefore, this solution will contain about 0.5 weight percent fly ash which should not present any handling problems.

Prior to entering the absorber system, the effluent stack gases from the cyclones are cooled from 300°F to 167°F by a circulating water system and the heat removed is then used to reheat the gases downstream of the scrubbers to obtain the buoyancy required for plume rise in the stack. In addition, less water is evaporated in this system as opposed to allowing the solution to directly cool the 300°F stack gas.

Sulfur dioxide is removed in the absorbers by the aqueous sodium sulfite-bisulfite solution. The liquid recirculation rate of the scrubbing solution is scaled down from that used in the 1400 MW plant and adjusted for the sulfur values in the Kellogg design case. This "scaling" down factor is used throughout the zinc oxide process to determine liquid and gas rates and the heat duties. The absorbers used for removing the SO_2 are four stage Impinjet$^{T.M.}$ wet scrubbers (manufactured by the W. W. Sly Mfg. Co.) which are assumed to give the desired 90% removal. Based on the vendor's recommendations, an allowable superficial gas velocity of 500 ft/min was used in sizing the tower area. The tower operates at 122°F with the 14% solution of sodium sulfite/bisulfite. Since enthalpy data were not available on the absorption system, it was assumed that the absorbers are in heat balance. Sodium sulfate is formed by oxidation of sulfite in the absorbers. The molar ratio of sulfite to sulfate is assumed to be 3/1 which is the same as that used by Envirogenics (1).*

The spent solution leaving the absorbers is mixed with a calcium sulfite solution in the clarifier L-1. This unit size was scaled down from the one given by Envirogenics since no settling data are given in their report (1). Clear liquid leaving the clarifier is sent to the ZnO tanks where $ZnSO_3$ is formed. Again, the processing equipment needed for formation, crystallization and thickening of $ZnSO_3$ is scaled down from the Envirogenics report because of the absence of reported data on the reaction of ZnO to form $ZnSO_3$ and crystal growth rate. Superdecanting centrifuges are assumed to be capable of separating the $ZnSO_3$ crystals from the lean solution of sulfite-bisulfite. This lean solution is refortified with soda ash to make up losses in a lean solution surge tank which was scaled down directly from that used in the larger plant. The solution in the lean solution surge tank is pumped to the stack gas absorbers, thus completing the cycle.

Wet crystals discharged from the centrifuges contain 17% free water which is evaporated in a direct dryer to produce the dry crystals of $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$. Drying is carried out concurrently with combustion gases entering at 700°F and the dried solids leaving the dryer at 200°F. No liberation of SO_2 would take place in the dryer since only free water is evaporated. The dryer duty used for design was scaled down from the larger plant owing to the lack of specific heat data on $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$. However, as an approximate check, the dryer duty was estimated independently and the estimated and scaled-down heat requirements were in close agreement.

The Envirogenics process flow sheet shows a cyclone to recover the fines in the effluent flue gas from the dryer and a hammer mill on the solids discharge stream. Since particle size distribution data are not available for the dryer effluent solids and, since "clinkers" may be formed in the dryer, use of the cyclone and grinding system was assumed necessary. The cyclone was scaled down from the Envirogenics case. However, a grinding mill system was substituted for the hammer mill shown by Envirogenics in order to produce a finer particle size, viz., 70% minus 200 mesh.

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* Refer to references at end of section.

The dried zinc sulfite (hydrated) is feed to a tripping belt feeder so that the $ZnSO_3$ can be distributed to a 5 bin hopper which in turn is used to feed the 5 indirect kilns. Thus each kiln has an independently controlled solids feed.

The $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$ is indirectly calcined at the same temperature used by Envirogenics (850°F). Five of these calciners are required to handle the total solids flow since maximum kiln size available is limited by the need for tight seals to prevent leakage of air into the system which would produce sulfate. The estimated heat requirement of the calciner was lower than that obtained by scaling down the larger plant. Consequently, since enthalpy data were not available, the scaled-down value (larger) was used to insure an adequate design.

A cyclone is needed on the calciner effluent gas to recover the entrained zinc oxide since 70% of the precalcined particles were assumed to be less than 200 mesh. It was further assumed, since no specific data were available, that essentially all the calcined particles were greater than 40 microns, thus resulting in a collection efficiency of about 100% in the cyclone. However, if significant quantities of particles less than 40 microns are produced, other means of dust collection probably would be required to keep zinc oxide losses low.

An absorber tower is used to cool the gases leaving the calciner cyclone. This absorber is simply a packed tower sized to give the gas cooling and water absorption required. Recirculated water is used as the absorbent and the heat gained in the water is removed by an external exchanger.

The SO_2 leaving the water absorber system is in part sent to the acid plant for conversion to concentrated (98.5%) sulfuric acid. Product acid storage equivalent to 30 days' production was assumed necessary to allow for continuous plant operation even if modest delays in shipping (e.g., R.R. strike) were encountered. The unloading system is designed such that a day's production of sulfuric acid can be pumped out of storage in six hours.

The remaining SO_2 is recycled and used to dissolve the insoluble $CaSO_3$ in the gasifier. This is accomplished in a continuous stirred tank reactor equipped with a turbine-type agitator. This reactor holding time is based on that used by Envirogenics.

Liquid leaving the gasifier contains insoluble $CaSO_4$ and fly ash. This slurry is thickened in a waste thickener which has been sized by scaling.

Clean liquor from the waste thickener is sent to the liming tanks where insoluble $CaSO_3$ is formed as shown by the process reactions given earlier. These liming vessels are agitated and have simple covers. Two reactors in series are used to minimize by-passing of the CaO and to insure formation of the $CaSO_3$.

A tilting pan filter with three water wash stages is used to recover the occluded liquor from the thickened waste slurry. Sizing of this filter is based on filtration data for gypsum. Waste solids are sluiced to a slurry tank to give a 10 wt % slurry and the slurried waste is pumped to a settling pond.

Solid hopper feeder systems for make-up ZnO and soda ash are sized to hold a week's supply of feed. To insure proper control, weigh feeders are used for adding the make-up ZnO and soda ash to the system. The lime storage is for one week but the lime feeder-hopper is only one day. Lime is fed into the liming tank using a weigh feeder to insure proper control. To insure that the dried $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$ is properly distributed to each of the five calcining kilns, weigh feeders are again used. Delivery of make-up solids is assumed to be by truck with pneumatic unloading and all solids hoppers are vented to the atmosphere through bag filters for dust control.

4. Process Appraisal

The wet scrubbing zinc oxide process has been shown to be technically feasible (3). Although a process flow sheet and material balance were prepared and major equipment were sized by Envirogenics (1), additional data are required in every facet of this process before a definitive design can be made. The major advantages and disadvantages of this process will be given before discussing those areas which need additional information.

a. Advantages

- Wet scrubbing of the flue gas eliminates the need for high efficiency precipitators. Fly ash not removed in the precipitator is removed with the scrubbing solution.
- Calcination of a sulfite ($ZnSO_3 \cdot 2\text{-}1/2\ H_2O$) to produce by-product SO_2 and regenerated ZnO is carried out at a relatively low temperature.
- High degrees of SO_2 removal from the flue gas should be readily obtained.
- Concentrated H_2SO_4 is produced rather than dilute acid as in some processes.

b. Disadvantages

- Presence of nitrogen oxides in the flue gas causes the loss of sodium values in the scrubbing liquor.
- Oxidation of sulfite to sulfate results in a loss of calcium thus increasing both operating costs and the quantity of waste.
- Wet scrubbing cools and saturates the flue gas and requires reheat to get plume rise.
- Disproportionation of zinc sulfite in the kilns forms zinc sulfide and represents a potential loss of zinc or will require expensive additional processing.
- By-product sulfuric acid is produced instead of elemental sulfur, thus complicating storage and handling problems.

c. General Considerations

The various individual steps in the zinc oxide process have been experimentally demonstrated (3). The literature contains some laboratory data which have been obtained on this process. Although the process concept has been demonstrated, additional processing and thermodynamic data are required in all areas of this process before a prototype demonstration unit can be designed in detail.

The thermodynamic requirements are as follows.

- Vapor pressure of sulfur dioxide over aqueous solutions of sodium sulfite-bisulfite. Some data are available in the literature but should be checked for thermodynamic consistency to determine if additional experimentation is required.
- Solubility data on the different precipitated salts, i.e., zinc sulfite, calcium sulfite, calcium sulfate.
- Heat of reaction data may be available in the literature.
- Specific heats of zinc sulfite and zinc oxide
- Heat of hydration of the zinc sulfite.

The different chemical processing steps of the process also must be studied experimentally. Processing studies are required in all the steps of the process and are as follows.

- Scrubbing

  As pointed out above, vapor pressure data of sulfur dioxide over the sodium sulfite-bisulfite system are required. In addition, processing studies must be made to obtain data on the effects of variables such as temperature and liquid-to-gas-rate on mass transfer rate. The effect of nitrogen oxides on the absorption step must be determined. Nitrogen oxides, oxygen and possibly fly ash can affect the amount of sulfate formed and the effect of these process variables must be more clearly defined.

- Liming Tank

  Particulate lime in suspension in the presence of sulfate ion can form a shell of calcium sulfate which hinders the hydration and dissolution reactions. The same phenomenon also can occur in the precipitation of zinc sulfite from zinc oxide. Unless particle size is properly controlled, full utilization of the zinc and calcium oxides will not be realized. Consequently quantities larger than stoichiometric must be used thereby increasing the solids load through the plant.

  This reaction must be studied to determine the reaction rate of the calcium oxide with the sodium bisulfite. Since the sulfate in solution can coat the calcium oxide, the effect of particle size on conversion (i.e., calcium oxide utilization) should be determined.

- Gasifier

  Temperature, pressure and sulfate concentration effects on dissolution of sulfite and precipitation of sulfate need to be determined.

- Mixer

  Rate data need to be determined experimentally on the formation of zinc sulfite, including the effects of temperature and sodium bisulfite concentration. Particle size of the zinc oxide may affect the conversion level owing to a coating of zinc sulfite on the particle surfaces. This effect must be understood to determine if greater than stoichiometric quantities are needed.

- Calciner

  Additional experimental data on the calcination of zinc sulfite are needed to enable proper design of the reactor. The flash-type calciner recommended by Field et al (3) may pose severe design problems. Solids transport data are required to determine if this reactor is desirable or if an indirect rotary kiln is preferable. In calcination, the degree of agglomeration and attrition of solids need to be understood to determine if grinders and cyclones also are required. The problem of disproportionation has in part been studied (2) but more detailed experimental data are required before this problem can be completely understood.

- Dryer

  Drying data on the wet zinc sulfite are needed since sizing the drying kiln depends on the heat transfer rate. Drying rate will depend on the hot gas circulation rate and the particle size distribution of the wet crystals. The quantity and size distribution of the fines produced by attrition and the degree of agglomeration of particles is needed for sizing the cyclone and grinding mill downstream of the dryer.

  In addition to the above basic areas of study, studies should also be made in the following.

- Miscellaneous

  Settling data are required for proper sizing of the clarifier, zinc sulfite thickener and waste thickener.

  The angle of repose and flow characteristics of the solids used in the process should be determined to provide design data for storage, feeding, and conveying equipment.

  The rheological properties of the thickened solids slurries should be determined to insure that pumps are properly designed.

In addition to the above studies made on the individual steps of this process, an integrated pilot plant should be operated to demonstrate the total system. Recycle streams may build up undesirable by-product which may necessitate bleed streams or additional processing.

REFERENCES

The process design and evaluation are based on the references stated below. No other sources of data were made available to Kellogg for this evaluation.

(1) Envirogenics Company, A Division of Aerojet-General Corp., Applicability of Aqueous Solutions to the Removal of SO_2 From Flue Gases, Final Report, Volume 1, Contract #PA 86-68-77, Submitted to National Air Pollution Control Administration (Oct. 1970).

(2) Ibid, Volume 2.

(3) Field, J. H., Brunn, L. W., Haynes, W. P. and Benson, H. B., Cost Estimate of Liquid Scrubbing Process for Removing Sulfur Dioxide From Flue Gases, Bureau of Mines, Report of Investigations 5469 (1959).

B. CHEMISTRY

In the zinc oxide process the stack gas is scrubbed countercurrently with a sodium sulfite solution. The sulfur dioxide in the stack gas reacts with the sodium sulfite to produce sodium bisulfite.

$$Na_2SO_3(l) + H_2O(l) + SO_2(g) \rightarrow 2NaHSO_3 \qquad (1)$$

The effluent from the scrubber is mixed with zinc oxide to form insoluble zinc sulfite and to regenerate sodium sulfite.

$$ZnO + 2NaHSO_3 + 1\text{-}1/2\ H_2O \rightarrow ZnSO_3 \cdot 2\text{-}1/2\ H_2O + Na_2SO_3 \qquad (2)$$

The solid zinc sulfite is separated and calcined to regenerate zinc oxide and produce sulfur dioxide in a concentrated form for recovery as such or conversion to elemental sulfur or sulfuric acid.

$$ZnSO_3 \cdot 2\text{-}1/2\ H_2O \rightarrow ZnO + SO_2 + 2\text{-}1/2\ H_2O \qquad (3)$$

Perhaps the most vexing problem of all bulk water scrubbing systems is the oxidation of the sulfur dioxide-sulfite system to a sulfur trioxide-sulfate system due to the presence of oxygen, nitrogen oxides and/or fly ash. This problem is of importance in an oxidation product in that sulfate ion, formed as an oxidation product in the scrubber, does not produce an insoluble zinc salt which can be regenerated to zinc oxide and, therefore, builds up in the scrubber by consuming effective Na_2O content. Some sulfate is also formed in the calciner which also finds its way into the scrubber. Data of Johnstone and Singh (2) show that the overall production of sulfate amounts to 10% whereas the Bureau of Mines reports a 14% overall production of sulfate.

A separate system is incorporated in this process to remove the sulfate by converting it to calcium sulfate.

$$2NaHSO_3(l) + CaO(s) \rightarrow Na_2SO_3(l) + CaSO_3 + H_2O \qquad (4)$$

$$CaSO_3(s) + H_2O(l) + SO_2(g) \rightarrow Ca(HSO_3)_2(l) \qquad (5)$$

$$Ca(HSO_3)_2(l) + Na_2SO_4(l) \rightarrow 2NaHSO_3(l) + CaSO_4 \qquad (6)$$

A side stream of the sulfate-containing scrubber solution is reacted with a less than stoichiometric quantity of calcium oxide to produce sodium sulfite and insoluble calcium sulfite. The solid calcium sulfite is further reacted with product sulfur dioxide to produce soluble calcium bisulfite. The above step provides the calcium ion concentration necessary to precipitate only calcium sulfate.

The solid calcium sulfate is separated to waste and the liquid bisulfite recycled to the liming step. Since only a portion of the sulfate ion is being removed there will be a steady state concentration of sulfate ion in the entire system.

Aside from the problem of oxidation of sulfite to sulfate in the calciner is the problem of the disproportionation reaction.

$$4ZnSO_3 \cdot 2\text{-}1/2\ H_2O \rightarrow 3ZnSO_4 + ZnS + 10H_2O \qquad (7)$$

The presence of zinc sulfite in this system would be detrimental to its operation since it will not decompose to zinc oxide, is difficult to remove and will not react with bisulfite solution. Therefore, any appreciable production of ZnS per pass will eventually use up all of the zinc oxide.

A systematic study of the disproportionation reaction shows that this reaction begins at 300°C, increase in rate with increasing temperature to 375°C and then decreases in rate with a further increase in temperature. According to Johnstone (1) at 350°C disproportionation occurs to the extent of 4%. Subsequent work (1) indicates that if the calcining is done in the presence of steam, no disproportionation occurs since the decomposition of $ZnSO_3 \cdot 2\text{-}1/2\ H_2O$ can be carried out at 290°C.

It has also been reported (1) that the maximum concentration of sodium ions in the scrubbing solution should be limited to 3.5 moles/100 moles of water to prevent the formation of the double salt of sodium and zinc sulfites.

$$6NaHSO_3 + 3ZnO + H_2O \rightarrow Na_2SO_3 \cdot 3ZnSO_3 \cdot 4H_2O + 2Na_2SO_3 \qquad (8)$$

It has been shown from other investigations that particulate lime in suspension in the presence of sulfate ion will form a shell or skin of calcium sulfate which hinders the hydration and dissolution reactions. As a consequence the full utilization of the lime is not realized. It is conceivable that this same phenomenon will occur during the precipitation of $ZnSO_3$ using particulate zinc oxide. The result of this condition is that the amount of solid zinc oxide which must be cycled will be much larger than the stoichiometric quantities required by the chemistry.

Others

Since the stack gas contains nitrogen oxides and fly ash as well as other gases, consideration should be given to the effect of these components on the overall process. Unfortunately, the chemistry of the interactions of NO + NO_2 with sulfite and bisulfite solutions is not clearly understood. There are data however that indicate that the presence of NO_2 in the gas stream greatly increases the rate of oxidation of sulfite to sulfate. There is no apparent effect of NO and NO_2 on the efficiency of absorption of sulfur dioxide.

Similarly the presence of fly ash has been shown to increase the rate of oxidation. The direct causes of the increase in the rate of oxidation have not been established but the end result is that the increase in the amount of sulfate produced obviously will require a larger clean-up process.

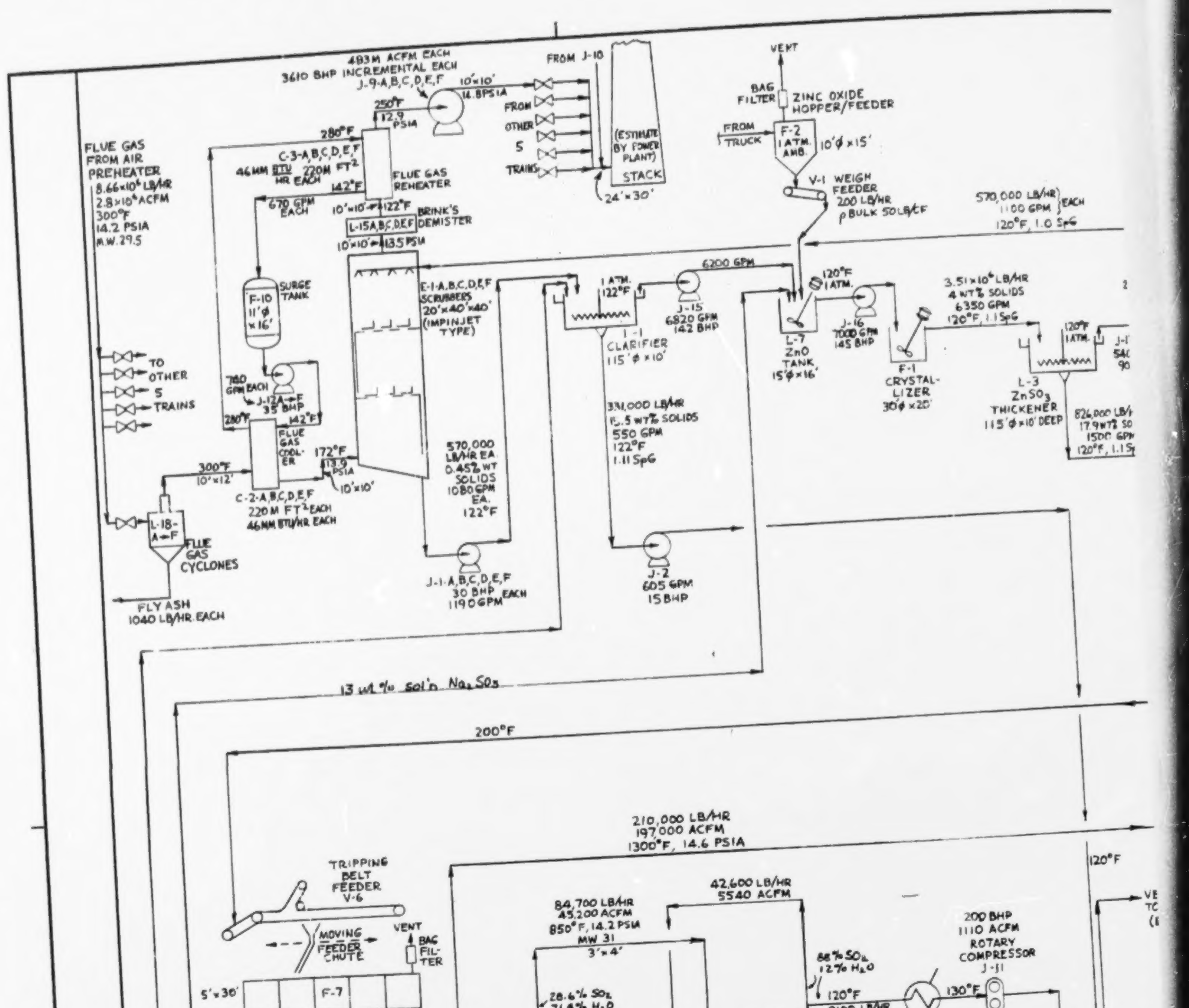
Summary

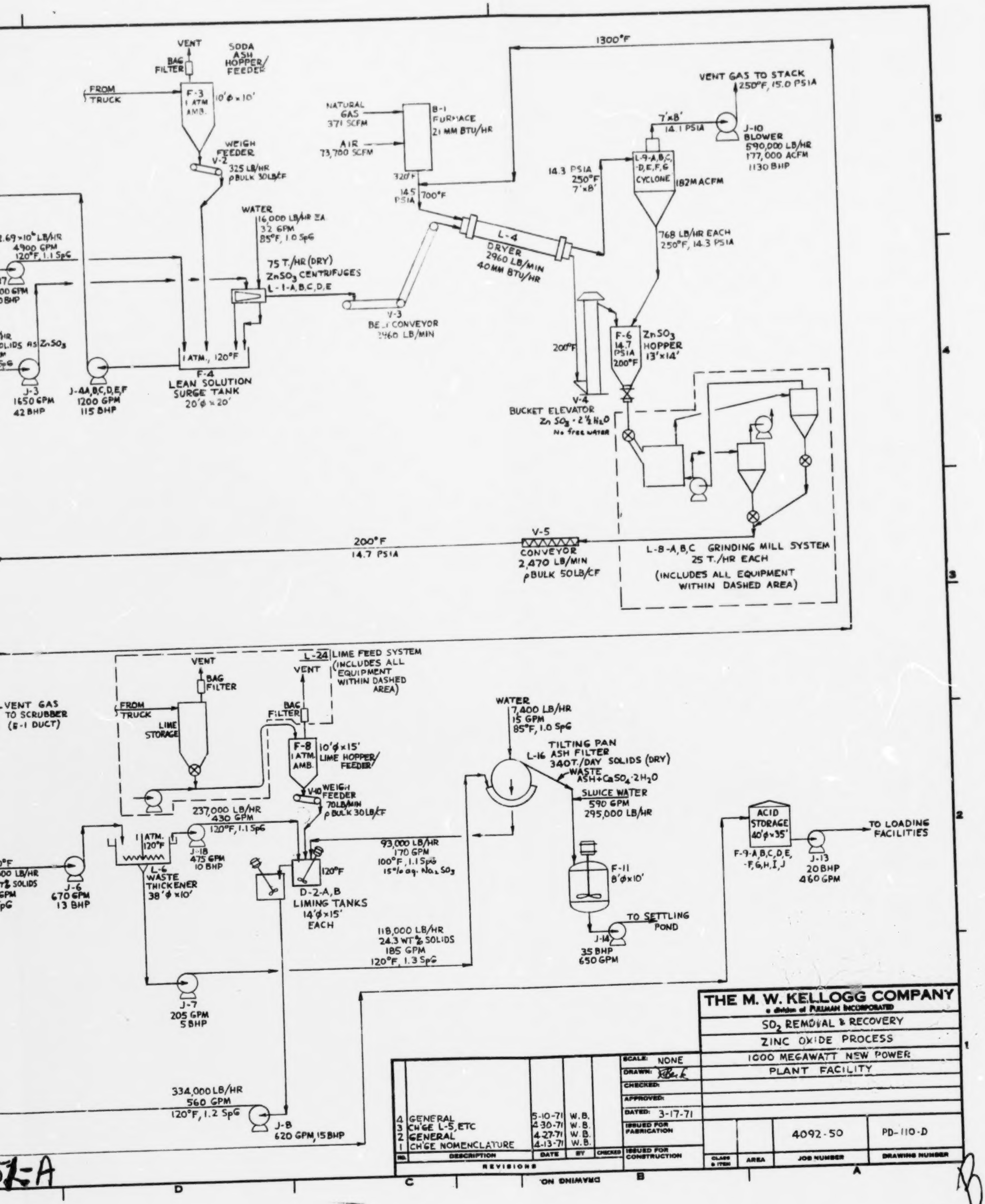
In summary, the zinc oxide process has the advantage of using a homogeneous scrubbing system as compared to a solids injection system and scrubbing with slurries. The major difficulties appear to be in the oxidation of sulfite to sulfate, the hydration of lime and the presence of nitrogen oxides and fly ash. A major process improvement would be to suppress or eliminate the oxidation reaction with a subsequent saving in process steps.

REFERENCES

(1) Envirogenics Company, A Division of Aerojet-General Corp., Applicability of Aqueous Solutions to the Removal of SO_2 From Flue Gases, Final Report, Volume 1, Contract #PA 86-68-77, Submitted to National Air Pollution Control Administration (October 1970).

(2) Ibid, Volume 2.


483M ACFM EACH
3610 BHP INCREMENTAL EACH
J-9-A,B,C,D,E,F
10'×10'
14.8PSIA
250°F
12.9 PSIA
280°F
C-3-A,B,C,D,E,F
46MM BTU HR EACH
220M FT²
142°F
FLUE GAS REHEATER
670 GPM EACH
10'×10'
122°F
BRINK'S DEMISTER
L-15A,B,C,D,E,F
10'×10'
13.5 PSIA
FROM J-10
FROM
OTHER
5
TRAINS
(ESTIMATE BY POWER PLANT)
STACK
24'×30'
FLUE GAS FROM AIR PREHEATER
8.66×10⁶ LB/HR
2.8×10⁶ ACFM
300°F
14.2 PSIA
M.W. 29.5
SURGE TANK
F-10
11'ϕ ×16'
780 GPM EACH
J-12A→F
35 BHP
280°F
142°F
FLUE GAS COOLER
E-1-A,B,C,D,E,F
SCRUBBERS
20'×40'×40'
(IMPINJET TYPE)
TO
OTHER
5
TRAINS
300°F
10'×12'
172°F
13.9 PSIA
10'×10'
C-2-A,B,C,D,E,F
220M FT² EACH
46MM BTU/HR EACH
570,000 LB/HR EA.
0.45% WT SOLIDS
1080 GPM EA.
122°F
L-18-A→F
FLUE GAS CYCLONES
FLY ASH
1040 LB/HR. EACH
J-1-A,B,C,D,E,F
30 BHP EACH
1190 GPM
1 ATM.
122°F
J-15
6820 GPM
142 BHP
6200 GPM
L-1
CLARIFIER
115'ϕ ×10'
331,000 LB/HR
15.5 WT% SOLIDS
550 GPM
122°F
1.11 SpG
J-2
605 GPM
15 BHP
VENT
BAG FILTER
ZINC OXIDE HOPPER/FEEDER
FROM TRUCK
F-2
1 ATM. AMB.
10'ϕ ×15'
V-1 WEIGH FEEDER
200 LB/HR
ρ BULK 50LB/CF
570,000 LB/HR
1100 GPM
EACH
120°F, 1.0 SpG
120°F
1 ATM.
L-7
ZnO TANK
15'ϕ×16'
J-16
7000 GPM
145 BHP
F-1
CRYSTAL-LIZER
30'ϕ ×20'
3.51×10⁶ LB/HR
4 WT% SOLIDS
6350 GPM
120°F, 1.1 SpG
120°F
1 ATM.
L-3
ZnSO₃
THICKENER
115'ϕ×10' DEEP
826,000 LB/
17.9 WT% SO
1500 GPM
120°F, 1.1 S
13 wt % sol'n Na₂SO₃
200°F
210,000 LB/HR
197,000 ACFM
1300°F, 14.6 PSIA
TRIPPING BELT FEEDER
V-6
MOVING FEEDER CHUTE
VENT
BAG FILTER
5'×30'
F-7
TO OTHER 4 KILNS
NAT. GAS
410 SCFM
AIR
3280 SCFM
WEIGH FEEDER
V-7-A,B,C,D,E
494 LB/MIN EA.
ρ BULK 50LB/CF
14.7 PSIA, 850°F
L-5-A,B,C,D,E
INDIRECT KILN
23MM BTU/HR EACH
FROM L-5-B,C,D,E
F-12
GAS-SOLIDS SEPARATOR
20'ϕ ×20'
3'×4'
L-10-A,B
CYCLONE
20 LB/MIN EACH
84,700 LB/HR
45,200 ACFM
850°F, 14.2 PSIA
MW 31
3'×4'
28.6% SO₂
71.4% H₂O
850°F
14.7 PSIA
ZnO
V-8
CONVEYOR
1840 LB/MIN
L-17
H₂SO₄
PLANT
42,600 LB/HR
5540 ACFM
88% SO₂
12% H₂O
120°F
9100 LB/HR
1140 ACFM
C-4
10 FT²
15,000 BTU/HR
130°F
200 BHP
1110 ACFM
ROTARY COMPRESSOR
J-11
51,700 LB/HR
6680 ACFM
120°F 13.7 PSIA
MW 58.5
120°F
120°F
E-2
ABSORBER
10'ϕ × 28'
630 CF PACKING
1.33×10⁶ LB/HR
2654 GPM
120°F
1.0 SpG
C-1
COOLER
53MM BTU/HR
5,250 FT²
850°F
14.1 PSIA
160°F
1.36×10⁶ LB/HR
2720 GPM
160°F
1.0 SpG
J-5
2990 GPM
80 BHP
33,100 LB/HR
66 GPM
160°F
1.0 SpG
120°F
VE
TC
(I
30 PSIA
120 °F
D-1
GASIFIER
15'ϕ×15'
120°F
340,000 L
11.7 WT% SC
610 GPM
1.1 SpG
367,000 LB/HR
630 GPM
125°F, 1.2 SpG
62,900 LB/HR 98.5 WT% H₂SO₄
25
H
G
F
E


VENT
BAG FILTER
SODA ASH HOPPER/ FEEDER
FROM TRUCK
F-3 1 ATM AMB.
10'ϕ × 10'
WEIGH FEEDER
V-2
325 LB/HR
ρBULK 30LB/CF
WATER
16,000 LB/HR EA
32 GPM
85°F, 1.0 SpG
75 T./HR (DRY)
ZnSO3 CENTRIFUGES
L-1-A,B,C,D,E
2.69×10⁶ LB/HR
4900 GPM
120°F, 1.1 SpG
00 GPM
0 BHP
HR
OLIDS AS ZnSO3
F-4
LEAN SOLUTION SURGE TANK
20'ϕ × 20'
1 ATM., 120°F
J-3
1650 GPM
42 BHP
J-4A,B,C,D,E,F
1200 GPM
115 BHP
NATURAL GAS
371 SCFM
AIR
73,700 SCFM
B-1
FURNACE
21 MM BTU/HR
320°F
14.5 PSIA
700°F
1300°F
L-4
DRYER
2960 LB/MIN
40 MM BTU/HR
V-3
BELT CONVEYOR
2960 LB/MIN
VENT GAS TO STACK
250°F, 15.0 PSIA
7'×8'
14.1 PSIA
J-10
BLOWER
590,000 LB/HR
177,000 ACFM
1130 BHP
14.3 PSIA
250°F
7'×8'
L-9-A,B,C,-D,E,F,G
CYCLONE
182M ACFM
768 LB/HR EACH
250°F, 14.3 PSIA
200°F
F-6
14.7 PSIA
200°F
ZnSO3 HOPPER
13'×14'
V-4
BUCKET ELEVATOR
ZnSO3 · 2½ H2O
No free water
200°F
14.7 PSIA
V-5
CONVEYOR
2,470 LB/MIN
ρBULK 50LB/CF
L-8-A,B,C GRINDING MILL SYSTEM
25 T./HR EACH
(INCLUDES ALL EQUIPMENT WITHIN DASHED AREA)
VENT GAS TO SCRUBBER (E-1 DUCT)
VENT
BAG FILTER
FROM TRUCK
LIME STORAGE
L-24 LIME FEED SYSTEM (INCLUDES ALL EQUIPMENT WITHIN DASHED AREA)
VENT
BAG FILTER
F-8 1 ATM. AMB.
10'ϕ×15'
LIME HOPPER/ FEEDER
V-10 WEIGH FEEDER
70LB/MIN
ρBULK 30LB/CF
237,000 LB/HR
430 GPM
120°F, 1.1 SpG
1 ATM. 120°F
J-18
475 GPM
10 BHP
L-6
WASTE THICKENER
38'ϕ ×10'
°F
00 LB/HR
T% SOLIDS
GPM
pG
J-6
670 GPM
13 BHP
120°F
D-2-A,B
LIMING TANKS
14'ϕ×15' EACH
93,000 LB/HR
170 GPM
100°F, 1.1 SpG
15% aq. Na2SO3
118,000 LB/HR
24.3 WT% SOLIDS
185 GPM
120°F, 1.3 SpG
J-7
205 GPM
5 BHP
334,000 LB/HR
560 GPM
120°F, 1.2 SpG
J-8
620 GPM, 15 BHP
WATER
7,400 LB/HR
15 GPM
85°F, 1.0 SpG
TILTING PAN ASH FILTER
L-16
340T./DAY SOLIDS (DRY)
WASTE ASH+CaSO4·2H2O
SLUICE WATER
590 GPM
295,000 LB/HR
F-11
8'ϕ×10'
TO SETTLING POND
J-14
35 BHP
650 GPM
ACID STORAGE
40'ϕ×35'
F-9-A,B,C,D,E,-F,G,H,I,J
J-13
20 BHP
460 GPM
TO LOADING FACILITIES
5
4
3
2
1
D
C
B
A
DRAWING NO.
51-A

THE M. W. KELLOGG COMPANY
a division of PULLMAN INCORPORATED

SO_2 REMOVAL & RECOVERY

ZINC OXIDE PROCESS

1000 MEGAWATT NEW POWER

PLANT FACILITY

SCALE: NONE

DRAWN: R.Beck

CHECKED:

APPROVED:

DATED: 3-17-71

ISSUED FOR FABRICATION

ISSUED FOR CONSTRUCTION

NO.	DESCRIPTION	DATE	BY	CHECKED
4	GENERAL	5-10-71	W.B.	
3	CH'GE L-5, ETC	4-30-71	W.B.	
2	GENERAL	4-27-71	W.B.	
1	CH'GE NOMENCLATURE	4-13-71	W.B.	

REVISIONS

CLASS & ITEM	AREA	JOB NUMBER	DRAWING NUMBER
		4092-50	PD-110-D

CITRATE PROCESS

A. PROCESS

1. Process Description (See MWK Dwg. No. PD-121-D)

In the citrate process, SO_2 is removed from the flue gas by contacting the gas stream with an aqueous solution of citric acid and sodium carbonate. The SO_2, which complexes with the citrate ion, is then reacted with H_2S to precipitate sulfur. After separation of the sulfur from the citrate solution, about one-third of the sulfur, equivalent to the amount absorbed less losses, is removed as product while two-thirds are converted to H_2S for recycle.

Flue gas from the air preheater is split into 6 parallel trains and cooled from 300°F to 157°F in coolers C-1 A-F. The gas is then scrubbed with an ash slurry in E-1 A-F to remove 98% of the fly ash and all of the SO_3, while cooling the gas to 105°F. A low gas temperature and minimal SO_3 content are important for efficient SO_2 removal in the subsequent absorption step. Part of the slurry from E-1 A-F is purged to D-5 where it is neutralized with limestone prior to disposal as waste. The bulk of the slurry is recycled through coolers C-3 A-F to the scrubbers.

Cooled flue gas from E-1 A-F is sent to absorbers E-2 A-F where 90% of the SO_2 is removed from the gas by contact with a citric acid/sodium carbonate solution at 115°F. The cleaned flue gas leaves the absorbers saturated with water at 107°F, is reheated in C-3 A-F to 250°F (using the heat recovered from the flue gas in C-1 A-F) and compressed in J-1 A-F to stack pressure before being exhausted to the atmosphere. Water, which is produced in the H_2S-SO_2 reaction step, is removed from the citrate solution in the absorbers by saturating the flue gas through contact with the warmer liquid.

The SO_2-rich solution from E-2 A-F is reacted with H_2S in D-1 A-F to precipitate sulfur according to the reaction:

$$SO_2 + 2H_2S \rightleftarrows 3S + 2H_2O$$

Part of the solution bypasses D-1 A-F and is combined with the bottoms to react with any dissolved H_2S which leaves the reactor. The resultant sulfur slurry is thickened from 0.5% solids to 10% solids in thickener L-3 and centrifuged in L-4A-G to remove all solids. The filtrate from L-4A-G is combined with the thickener overflow and sent to citrate feed tank F-2 for recycle to the absorbers. Residual solids in the solution are removed in line filters L-5 A,B.

Wet cake from centrifuges L-4A-G is conveyed to tank F-4 where it is re-slurried with part of the thickener underflow. This slurry, containing 33.3% solids, is heated in C-6 from 117°F to 280°F, thereby melting the sulfur. Phase separation of the liquid sulfur and the residual citrate solution occurs in F-5. The citrate solution is removed, cooled to 120°F in C-4, and pumped back to the feed tank F-2. Any SO_2 dissolved in the citrate solution from F-4, and released by heating, is vented from F-5 back to the absorbers E-2.

Liquid sulfur from F-5 contains the fly ash not removed in E-1A-F. This stream is centrifuged in L-6A,B. The ash is slurried in water in tank F-13 and pumped to waste disposal. Purified sulfur from L-6A,B is combined with recovered sulfur from sulfur separator F-1. About one-third of the total sulfur is pumped to storage as product while the remainder is recycled for conversion to H_2S. The net sulfur product equals the total sulfur removed from the flue gas less losses.

Recycle sulfur, at 276°F, is heated to 550°F in sulfur preheater F-6, using a non-flow system in order to circumvent the peculiar viscosity characteristics of sulfur in the intervening temperature range. Sulfur from F-6 is vaporized and superheated to 1200°F in B-1, which also preheats a methane feed stream to 759°F. The two streams are combined and fed to carbon disulfide reactor at 1165°F and 40 psia where the following reaction occurs over a silica gel catalyst:

$$CH_4 + 4S \rightleftarrows CS_2 + 2H_2S$$

At the process conditions indicated, 90% of the methane is converted and the reaction is slightly exothermic.

The reactor effluent, at 1200°F, is used to preheat sulfur in F-6, after which it is cooled in a series of heat exchangers (C-7, C-8, C-9) to condense unreacted sulfur for recycle. Condensed sulfur is removed from the gas in sulfur separator F-1 and the effluent gas, after heating to 600°F, is combined with superheated steam and fed to the hydrolyzer D-4 at 493°F and 32.5 psia.

In D-4, CS_2 is hydrolyzed over an activated alumina catalyst according to the following reaction:

$$CS_2 + 2H_2O \rightleftarrows 2H_2S + CO_2$$

About 98% of the CS_2 is converted, and the temperature of the reaction is controlled at 600°F by generating steam. The effluent is cooled to 200°F in a series of heat exchangers (C-10, C-11, C-12).

In addition to that produced in D-4, steam is also generated in exchangers C-8 and C-11. The combined steam from these vessels is used in C-6 to melt sulfur. A balance is maintained between the steam generated and the steam required, resulting in a closed-loop system.

The cooled gas from C-12 is fed to reactors D-1 A-F where the H_2S-SO_2 reaction occurs. The effluent gas from D-1 containing both CS_2 and H_2S, is sent to absorber D-2A or D-2B which removes CS_2 by adsorption on activated carbon. The resulting gas stream is vented to stack through E-2A absorber which removes H_2S by reaction with the SO_2-rich citrate solution. This results in precipitation of some sulfur in the absorber. Adsorbed CS_2 in D-2A, B is removed with superheated steam and recycled to hydrolyzer D-4.

To remove sulfate formed either in the process or via SO_3 carry-over to the absorber, a purge stream is taken from the recovered citrate solution and pumped by J-11 to neutralizer D-5 before disposal. Make-up solution from F-3 is added to feed tank F-2 as required.

2. Process Design Bases

General design criteria used in evaluating this process, which is designed for installation in a new 1000 MW power plant, are those given elsewhere in this report as the basic criteria for all the present evaluations. The process design and material balance shown on Dwg. PD-121-D for the citrate process are based primarily on brief status reports and summaries of laboratory and pilot plant tests by the U.S. Bureau of Mines, including equilibrium data for the SO_2-absorption step. Basic design data for the sulfur recycling step, i.e., the conversion of sulfur to H_2S for recycle to the sulfur reactor, were lacking however, and these were obtained from the literature (1,2,3). Major design bases are listed below.

a. Absorbers E-2 A-F

gas inlet temperature	105°F
citrate solution inlet temperature	115°F
SO_2 removal from gas	90%
SO_2 loading on solution	4.3 gms SO_2/l solu (approx)
citric acid concentration	0.87 gm moles/l (approx)
Na/citric acid ratio	5.3 atoms/mole (approx)

b. Sulfur Reactors D-1 A-F

SO_2 conversion	100%
excess H_2S	5%
inlet superficial gas velocity (nominal)	0.1 fps
liquid residence time	10 minutes

c. Carbon Disulfide Reactor D-3

temperature	1200°F
space velocity (SCFH gas/CF catalyst)	560
catalyst	silica gel
methane purity	100%
methane conversion	90%
excess sulfur	10%

d. Hydrolyzer D-4

temperature	600°F
contact time	0.4 seconds
catalyst	activated alumina
carbon disulfide conversion	98%
excess steam	100%

3. Process Design Rationale

The citrate process has been developed through initial pilot plant stages by the U.S. Bureau of Mines. However, studies have been done primarily on smelter gases containing 1-3 mole percent SO_2 rather than on flue gases having a low SO_2 content. The information received, which contains equilibrium data on SO_2 absorption by solutions of citric acid/sodium citrate, also suggests that the major experimental effort has been directed towards the absorption step. Although the pilot plant has demonstrated sulfur recovery and recycle of the citrate solution, no attempt was made to recycle sulfur via conversion to H_2S.

The present process design is based, as far as possible, on the results of laboratory and pilot plant studies by the Bureau of Mines. Where necessary, process conditions were adjusted from those indicated by the U.S.B.M. to reflect the lower SO_2 gas concentration and other pertinent process factors that apply when treating power plant stack gases.

Prior to absorption of SO_2 by the citrate solution, SO_3 must be removed from the flue gas to minimize sulfate build-up in the recirculating solutions. This is done by scrubbing the gas with water, which also serves to remove fly ash while cooling the gas to 105°F.

For efficient absorption, temperatures in the absorber should be kept as low as possible. However, other factors such as gas cooling and reheat requirements resulted in the selection of a gas temperature of 105°F as a practical minimum. The solution temperature was chosen not only to allow absorption to occur, but also to provide a slight thermal driving force which serves to heat and saturate the gas, thereby removing water which is formed elsewhere in the process. At the temperatures selected, equilibrium curves show that citrate solution loadings of greater than 5 gms SO_2/liter solution can be achieved. The design loading of 4.3 gms SO_2/liter solution represents roughly an 80% approach to equilibrium.

Sulfate which is formed in the process must be continually purged from the system. In order to reduce the accompanying loss of citric acid to an acceptable level, it was assumed that sulfate could be allowed to build up to a high level in the solution before being purged. The required pH could be maintained by addition of soda ash. This scheme results in approximately the same citric acid concentration as that used by the Bureau of Mines (0.87 molar vs. 1.0 molar), but a higher sodium to citric acid ratio (5.3 vs. 1.5). If this does not prove to be feasible, the purge stream would have to be treated to remove sulfate before being returned to the process. It is not expected that this would have any significant effect on either process operation or economics.

Very little information was available for the design of the sulfur reactor, where sulfur is precipitated by reaction of SO_2 and H_2S. The Bureau of Mines states that the required residence time of the loaded citrate solution is about 10 minutes and that reaction occurs in a stirred, closed vessel. This was used for design, and it was assumed that 5% excess H_2S would keep a sufficient high back pressure of H_2S over the solution to drive the reaction to completion.

Some H_2S may dissolve in the citrate solution in the sulfur reactor. To eliminate its presence (and the possibility of its release) downstream in the process, a by-pass stream containing dissolved SO_2 is mixed with the reactor bottoms prior to thickening, thereby converting any H_2S present to sulfur.

H_2S will also leave the reactor in the gas phase. It is expected that this stream could be vented through the absorber, thus reacting the H_2S to extinction. This precipitates sulfur in the absorber, and its effect on tower operation is not known.

The H_2S required in the sulfur reactor is produced by the hydrolysis of carbon disulfide, CS_2. The behavior of residual CS_2 in the sulfur feed gas is not known. Presumably it will not react in the sulfur reactors, but will be carried out in the effluent gas. The CS_2 must be removed from the gas prior to venting, and one method of achieving this, viz., adsorption on activated charcoal, is shown on the flow sheet. The effects and behavior of other sulfur compounds, such as COS, which may be present in the reactor feed gas also are uncertain.

Since the Bureau of Mines has not recycled sulfur (as H_2S) in the pilot plant, no information was obtained from them for the design of this system. Several approaches could be taken, including the following possible routes:

1) natural gas reforming followed by sulfiding
2) single-step reaction of methane, steam, and sulfur
3) two-step reaction system consisting of reaction between methane and sulfur to form CS_2 and H_2S, followed by hydrolysis of the CS_2 to H_2S.

Some information for the design of the latter two was available in the literature, and the two-step system was selected for the present flow sheet design. This system minimizes formation of by-products such as COS and SO_2 by sulfiding methane in the absence of oxygen. The subsequent hydrolysis of CS_2 proceeds easily at moderate temperatures with high conversions. The system chosen represents a workable scheme, but no attempt at optimization was made.

Recovery of sulfur from the citrate solution and recycling of the solution has been demonstrated by the Bureau of Mines in the pilot plant. The present flow sheet basically follows the pilot plant scheme, although no design data were available for sizing purposes.

4. Process Appraisal

Based on the available information, the citrate process is a workable system for the efficient removal of SO_2 from power plant stack gases. Data do not appear to be missing for any critical areas which would cause the feasibility of the process to be questioned from a technical point of view.

Design data, in most instances, are lacking or incomplete and more development work is needed to adequately define process variables. Equilibrium data for SO_2 absorption are available, but these should be confirmed in the low range of SO_2 gas concentrations encountered in flue gas streams. Solubility and kinetic data are needed to establish the design of the sulfur reactor, and an investigation to determine the best commercial design (sprayed vessel, staged reactor, etc) should be made.

The H_2S generating system, although not piloted by the Bureau of Mines, is reasonably firm. According to the literature(3), the production of CS_2 from methane and sulfur has been commercialized. The subsequent hydrolysis of CS_2 is easily performed and represents no new technology.

Pilot plant testing on simulated flue gases containing fly ash is needed. Recycle of both citrate solution and sulfur should be demonstrated to determine the effects and levels of impurities in the system. It is also necessary to establish the permissible sulfate level in the citrate solution.

The preceeding points were mentioned to point out some of the deficiencies in existing design data. A confident commercial design could only be made after resolution of these deficiencies through further experimental work.

One advantage of the citrate process is that the sulfur is recovered in elemental form. It is more easily handled, stored, and marketed compared to other forms of sulfur (e.g. sulfuric acid) which are produced by some of the other SO_2-removal processes.

The citrate process should be easily adaptable to varying sulfur content in the power plant fuel as well as varying turndown ratios (corresponding to the cycling of power demand). Six separate trains on the front end of the process operate independently, and since the entire process with the exception of the H_2S generating section operates at about ambient temperature, start-up of the single train can be done easily by establishing circulation of the citrate solution. Shutdown is just as readily achieved. No heating or cooling periods are necessary in either case.

A major disadvantage of the process is that since absorption must be done cold (about 110-115°F) and in an SO_3-free environment, the gas must be cooled, scrubbed, and reheated before being discharged to stack. This requires extensive equipment and represents a significant part of the overall cost of the process.

Since fly ash is removed from the flue gas during the water scrubbing operation to remove SO_3, electrostatic precipitators are not required. For a new power plant, therefore, elimination of the precipitators represents a reduction in investment charged to the citrate process. The cost of the wet scrubbers would, of course, comprise a portion of the citrate investment. Retrofit to an existing power plant would pose no unusual problems, provided sufficient area were available, since the flue gas is withdrawn just upstream of the stack. Existing precipitators could be left in service or by-passed without adversely affecting operability of the citrate process.

REFERENCES

1. Bacon, R. F., and Boe, E. S., Ind. Eng. Chem., 37, 469-474 (1945).

2. Fisher, R. A., and Smith, J. M., Ind. Eng. Chem., 42, 704-709 (1950).

3. Folkins, H. O., Miller, E., and Hennig, H., Ind. Eng. Chem., 42, 2202-2207 (1950).

B. CHEMISTRY

The Bureau of Mines citrate process has as its core, the facile near quantitative reaction of sulfur dioxide with hydrogen sulfide at low temperature (50°C).

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$$

Since the hydrogen sulfide cannot be present in the flue gas absorption tower, a 'conveyor' is used to move the sulfur dioxide to a place where hydrogen sulfide can be present - the stirred closed reactor. The 'conveyor' is the citrate anion, produced from citric acid and sodium carbonate. This complexes with bisulfite (sulfur dioxide in water).

Other compounds will be formed in the hydrogen sulfide reactor, and if the pH is not carefully controlled, in the SO_2 absorber solution as well. Thiosulfate, polythionates and sulfate are likely the only ones of consequence and these products and their equilibria as outlined by the Bureau of Mines are consistent with the experimental work of other groups. For more efficient operation of the citrate process, they should be kept to as low a value as possible. It is indicated that they do not interfere in the process if their concentrations are low.

The pH plays a most important role in the citrate process and allied closely to this is the problem of sulfur trioxide carry-over into the SO_2 absorber due to incomplete gas washing. SO_3 carry-over will eventually lower the pH of the SO_2 absorbing solution and reduce its effectiveness as an SO_2 absorber (SO_2 is not absorbed in strong acid solutions). Strong acid tends to decompose thiosulfate and polythionates according to the reactions

$$8\ SSO_3^{=} + 16\ H^{+} \longrightarrow 8\ SO_2 + 8\ H_2O + S_8$$

$$S_4O_6^{=} + 2H^{+} + H_2O \longrightarrow H_2SO_4 + 1/4\ S_8 + SO_2 + H_2O$$

thus possibly precipitating sulfur in the SO_2 absorber. Sodium carbonate could be added to the SO_2 absorber to neutralize SO_3, but this action would be limited since it would lead to increased sulfate concentration in the absorbing liquor.

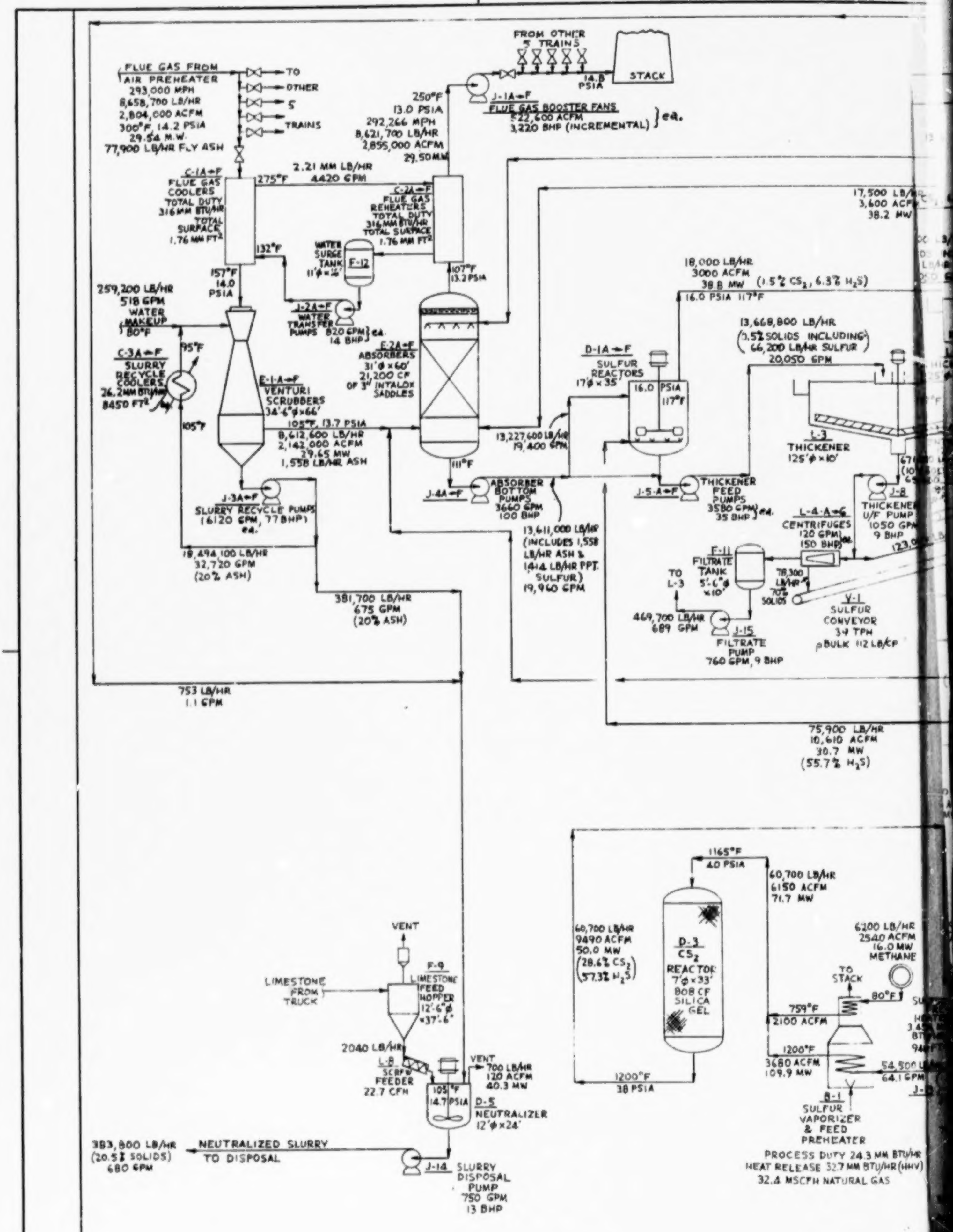
Sulfate can form via SO_3 carry over into the SO_2 absorber and also in the hydrogen sulfide reactor via the reaction

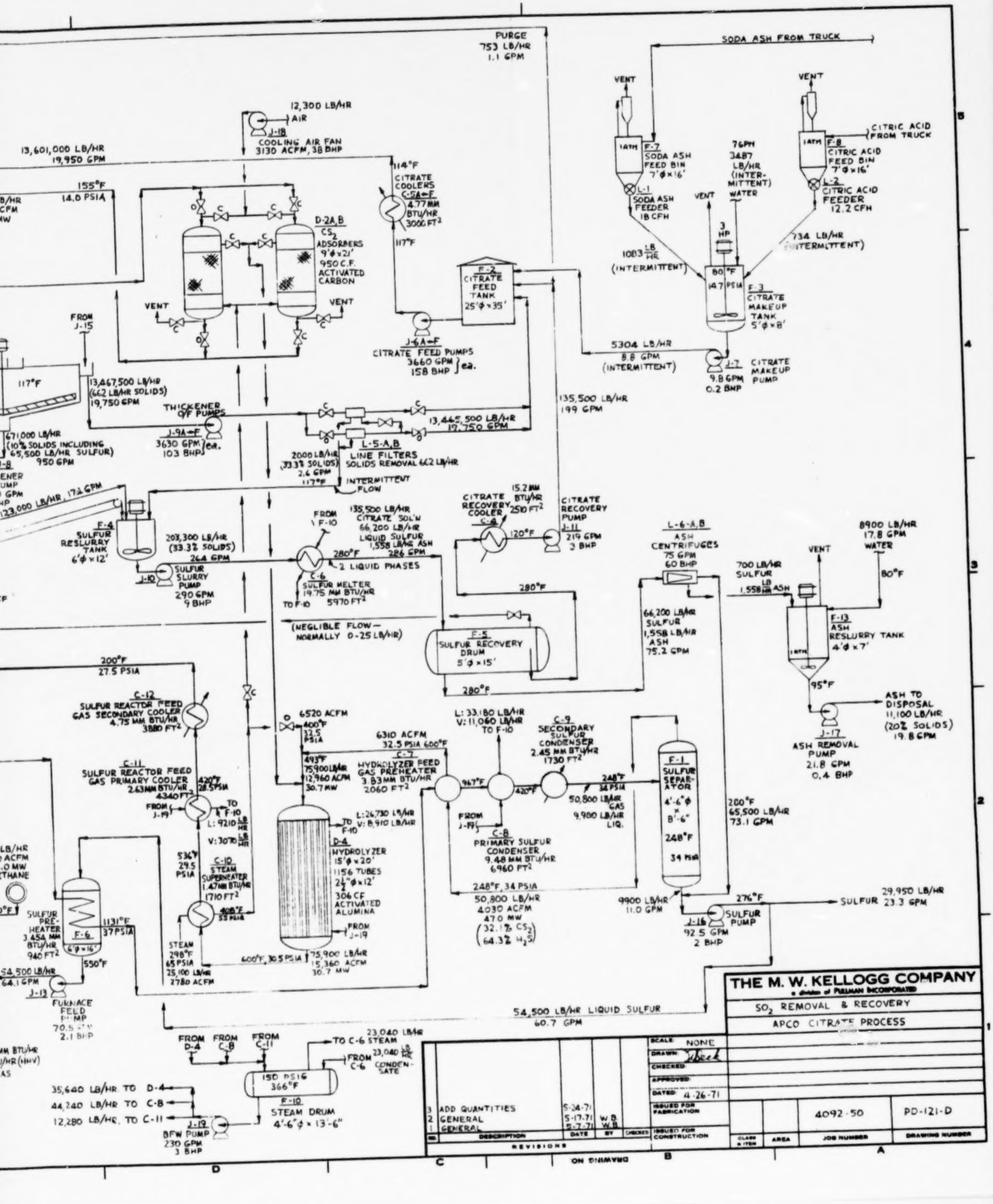
$$3HSO_3^{-} \longrightarrow 2SO_4^{=} + S + H^{+} + H_2O$$

and even if the carry-over problem is solved, it appears that there will be slight continuous sulfate buildup in the citrate liquor, eventually necessitating some treatment to remove sulfate.

Carbon dioxide is not expected to be absorbed in the citrate solution. The solution already has a high salt content (190 g/l citric acid, 80 g/l sodium carbonate, 20 g/l thiosulfate + smaller amounts of polythionate and sulfate), and a pH range 3.2 - 3.7. Water saturated with carbon dioxide has a pH of 3.7. Possible nitrogen oxide absorption in the citrate solution has not been studied but Bureau of Mines indicates it has begun investigating NO_x absorption in the gas washing and SO_2 absorption steps.

In conclusion, the SO_3 removal from the flue gas is an important procedure in this process. A scheme to remove sulfate also appears necessary. If these steps can be accomplished, the process (on a chemical basis) appears suitable for smelter gas clean-up.


FLUE GAS FROM
AIR PREHEATER
293,000 MPH
8,658,700 LB/HR
2,804,000 ACFM
300°F 14.2 PSIA
29.54 M.W.
77,900 LB/HR FLY ASH
TO
OTHER
5
TRAINS
FROM OTHER
5 TRAINS
14.8 PSIA
STACK
J-1A→F
FLUE GAS BOOSTER FANS
522,600 ACFM
3,220 BHP (INCREMENTAL) } ea.
250°F
13.0 PSIA
292,266 MPH
8,621,700 LB/HR
2,855,000 ACFM
29.50 MW
2.21 MM LB/HR
4420 GPM
275°F
C-1A→F
FLUE GAS
COOLERS
TOTAL DUTY
316 MM BTU/HR
TOTAL
SURFACE
1.76 MM FT²
C-2A→F
FLUE GAS
REHEATERS
TOTAL DUTY
316 MM BTU/HR
TOTAL SURFACE
1.76 MM FT²
132°F
WATER
SURGE
TANK
F-12
11'ø×16'
107°F
13.2 PSIA
157°F
14.0
PSIA
259,200 LB/HR
518 GPM
WATER
MAKEUP
80°F
J-2A→F
WATER
TRANSFER
PUMPS 820 GPM
14 BHP } ea.
95°F
C-3A→F
SLURRY
RECYCLE
COOLERS
26.2 MM BTU/HR
8450 FT²
105°F
E-1-A→F
VENTURI
SCRUBBERS
34'-6"ø×66'
E-2A→F
ABSORBERS
31'ø×60'
21,200 CF
OF 3" INTALOX
SADDLES
105°F, 13.7 PSIA
8,612,600 LB/HR
2,142,000 ACFM
29.65 MW
1,558 LB/HR ASH
111°F
J-3A→F
SLURRY RECYCLE PUMPS
(6120 GPM, 77 BHP)
ea.
18,494,100 LB/HR
32,720 GPM
(20% ASH)
381,700 LB/HR
675 GPM
(20% ASH)
753 LB/HR
1.1 GPM
J-4A→F
ABSORBER
BOTTOM
PUMPS
3660 GPM
100 BHP
13,611,000 LB/HR
(INCLUDES 1,558
LB/HR ASH &
1414 LB/HR PPT.
SULFUR)
19,960 GPM
13,227,600 LB/HR
19,400 GPM
D-1A→F
SULFUR
REACTORS
17'ø×35'
16.0 PSIA
117°F
18,000 LB/HR
3000 ACFM
38.8 MW (1.5% CS₂, 6.3% H₂S)
16.0 PSIA 117°F
17,500 LB/HR
3,600 ACFM
38.2 MW
13,668,800 LB/HR
(3.5% SOLIDS INCLUDING
66,200 LB/HR SULFUR)
20,050 GPM
L-3
THICKENER
125'ø×10'
J-5-A→F
THICKENER
FEED
PUMPS
3580 GPM
35 BHP } ea.
J-8
THICKENER
U/F PUMP
1050 GPM
9 BHP
L-4-A→G
CENTRIFUGES
120 GPM
150 BHP } ea.
F-11
FILTRATE
TANK
5'-6"ø
×10'
TO
L-3
78,300
LB/HR
70%
SOLIDS
V-1
SULFUR
CONVEYOR
34 TPH
ρBULK 112 LB/CF
469,700 LB/HR
689 GPM
J-15
FILTRATE
PUMP
760 GPM, 9 BHP
75,900 LB/HR
10,610 ACFM
30.7 MW
(55.7% H₂S)
1165°F
40 PSIA
60,700 LB/HR
6150 ACFM
71.7 MW
60,700 LB/HR
9490 ACFM
50.0 MW
(28.6% CS₂
57.3% H₂S)
D-3
CS₂
REACTOR
7'ø×33'
808 CF
SILICA
GEL
1200°F
38 PSIA
6200 LB/HR
2540 ACFM
16.0 MW
METHANE
TO
STACK
80°F
759°F
2100 ACFM
1200°F
3680 ACFM
109.9 MW
54,500
64.1 GPM
B-1
SULFUR
VAPORIZER
& FEED
PREHEATER
PROCESS DUTY 24.3 MM BTU/HR
HEAT RELEASE 32.7 MM BTU/HR (HHV)
32.4 MSCFH NATURAL GAS
VENT
F-9
LIMESTONE
FEED
HOPPER
12'-6"ø
×37'-6"
LIMESTONE
FROM
TRUCK
2040 LB/HR
L-8
SCREW
FEEDER
22.7 CFH
VENT
700 LB/HR
120 ACFM
40.3 MW
105°F
14.7 PSIA
D-5
NEUTRALIZER
12'ø×24'
383,800 LB/HR
(20.5% SOLIDS)
680 GPM
NEUTRALIZED SLURRY
TO DISPOSAL
J-14
SLURRY
DISPOSAL
PUMP
750 GPM
13 BHP
H
G
F
E


PURGE
753 LB/HR
1.1 GPM
SODA ASH FROM TRUCK
12,300 LB/HR
AIR
J-18
COOLING AIR FAN
3130 ACFM, 38 BHP
13,601,000 LB/HR
19,950 GPM
155°F
14.0 PSIA
114°F
CITRATE COOLERS
C-5A→F
4.77 MM BTU/HR
3000 FT²
117°F
D-2A,B
CS₂ ADSORBERS
9'Ø×21'
950 C.F. ACTIVATED CARBON
VENT
C
F-2
CITRATE FEED TANK
25'Ø×35'
J-6A→F
CITRATE FEED PUMPS
3660 GPM
158 BHP } ea.
VENT
1ATM
F-7
SODA ASH FEED BIN
7'Ø×16'
L-1
SODA ASH FEEDER
18 CFH
76PH
3487 LB/HR (INTER-MITTENT) WATER
3 HP
1083 LB/HR (INTERMITTENT)
80°F
14.7 PSIA
F-3
CITRATE MAKEUP TANK
5'Ø×8'
F-8
CITRIC ACID FEED BIN
7'Ø×16'
CITRIC ACID FROM TRUCK
L-2
CITRIC ACID FEEDER
12.2 CFH
734 LB/HR (INTERMITTENT)
5304 LB/HR
8.8 GPM
(INTERMITTENT)
J-7
CITRATE MAKEUP PUMP
9.8 GPM
0.2 BHP
FROM J-15
117°F
13,467,500 LB/HR
(662 LB/HR SOLIDS)
19,750 GPM
THICKENER O/F PUMPS
J-9A→F
3630 GPM
103 BHP } ea.
671,000 LB/HR
(10% SOLIDS INCLUDING 65,500 LB/HR SULFUR)
950 GPM
13,465,500 LB/HR
19,750 GPM
L-5-A,B
LINE FILTERS
SOLIDS REMOVAL 662 LB/HR
2000 LB/HR
(33.3% SOLIDS)
2.6 GPM
117°F
INTERMITTENT FLOW
135,500 LB/HR
199 GPM
123,000 LB/HR, 17.2 GPM
F-4
SULFUR RESLURRY TANK
6'Ø×12'
203,300 LB/HR
(33.3% SOLIDS)
264 GPM
J-10
SULFUR SLURRY PUMP
290 GPM
9 BHP
FROM F-10
135,500 LB/HR CITRATE SOL'N
66,200 LB/HR LIQUID SULFUR
1,558 LB/HR ASH
286 GPM
280°F
2 LIQUID PHASES
C-6
SULFUR MELTER
19.75 MM BTU/HR
5970 FT²
TO F-10
CITRATE RECOVERY COOLER
C-4
15.2 MM BTU/HR
2510 FT²
120°F
CITRATE RECOVERY PUMP
J-11
219 GPM
3 BHP
280°F
(NEGLIBLE FLOW— NORMALLY 0-25 LB/HR)
F-5
SULFUR RECOVERY DRUM
5'Ø×15'
280°F
L-6-A,B
ASH CENTRIFUGES
75 GPM
60 BHP
66,200 LB/HR SULFUR
1,558 LB/HR ASH
75.2 GPM
700 LB/HR SULFUR
1,558 LB/HR ASH
VENT
8900 LB/HR
17.8 GPM
WATER
80°F
F-13
ASH RESLURRY TANK
4'Ø×7'
95°F
ASH TO DISPOSAL
11,100 LB/HR
(20% SOLIDS)
19.8 GPM
J-17
ASH REMOVAL PUMP
21.8 GPM
0.4 BHP
200°F
27.5 PSIA
C-12
SULFUR REACTOR FEED GAS SECONDARY COOLER
4.75 MM BTU/HR
3880 FT²
6520 ACFM
400°F
32.5 PSIA
6310 ACFM
32.5 PSIA 600°F
493°F
75,900 LB/HR
12,960 ACFM
30.7 MW
C-7
HYDROLYZER FEED GAS PREHEATER
3.83 MM BTU/HR
2060 FT²
L: 33,180 LB/HR
V: 11,060 LB/HR
TO F-10
C-9
SECONDARY SULFUR CONDENSER
2.45 MM BTU/HR
1730 FT²
967°F
420°F
248°F
34 PSIA
50,800 LB/HR GAS
9,900 LB/HR LIQ.
F-1
SULFUR SEPARATOR
4'-6"Ø × 8'-6"
248°F
34 PSIA
C-11
SULFUR REACTOR FEED GAS PRIMARY COOLER
2.63 MM BTU/HR
4340 FT²
420°F
28.5 PSIA
FROM J-19
TO F-10
L: 9210 LB/HR
V: 3070 LB/HR
TO F-10
L: 26,730 LB/HR
V: 8,910 LB/HR
D-4
HYDROLYZER
15'Ø×20'
1156 TUBES
2½"Ø×12'
306 CF ACTIVATED ALUMINA
FROM J-19
FROM J-19
C-8
PRIMARY SULFUR CONDENSER
9.48 MM BTU/HR
6960 FT²
200°F
65,500 LB/HR
73.1 GPM
534°F
29.5 PSIA
C-10
STEAM SUPERHEATER
1.47 MM BTU/HR
1710 FT²
408°F
55 PSIA
248°F, 34 PSIA
50,800 LB/HR
4030 ACFM
47.0 MW
(32.1% CS₂)
(64.3% H₂S)
9900 LB/HR
11.0 GPM
276°F
J-16
SULFUR PUMP
92.5 GPM
2 BHP
SULFUR
29,950 LB/HR
23.3 GPM
LB/HR
ACFM
.0 MW
ETHANE
SULFUR PRE-HEATER
3.454 MM BTU/HR
940 FT²
F-6
6'Ø×16'
1131°F
37 PSIA
550°F
STEAM
298°F
65 PSIA
25,100 LB/HR
2780 ACFM
600°F, 30.5 PSIA
75,900 LB/HR
15,360 ACFM
30.7 MW
54,500 LB/HR
64.1 GPM
J-13
FURNACE FEED PUMP
70.5 GPM
2.1 BHP
54,500 LB/HR LIQUID SULFUR
60.7 GPM
MM BTU/HR
LB/HR (HHV)
AS
FROM D-4
FROM C-8
FROM C-11
TO C-6 STEAM
23,040 LB/HR
FROM C-6 CONDENSATE
23,040 LB/HR
150 PSIG
366°F
F-10
STEAM DRUM
4'-6"Ø × 13'-6"
35,640 LB/HR TO D-4
44,240 LB/HR TO C-8
12,280 LB/HR TO C-11
J-19
BFW PUMP
230 GPM
3 BHP
5
4
3
2
1
D
C
B
A

THE M. W. KELLOGG COMPANY
a division of PULLMAN INCORPORATED

SO₂ REMOVAL & RECOVERY

APCO CITRATE PROCESS

NO.	DESCRIPTION	DATE	BY	CHECKED
3	ADD QUANTITIES	5-24-71		
2	GENERAL	5-17-71	W.B.	
1	GENERAL	5-7-71	W.B.	

REVISIONS

SCALE: NONE
DRAWN: Zbeck
CHECKED:
APPROVED:
DATED: 4-26-71
ISSUED FOR FABRICATION
ISSUED FOR CONSTRUCTION

CLASS & ITEM	AREA	JOB NUMBER	DRAWING NUMBER
		4092-50	PD-121-D

DRAWING NO.